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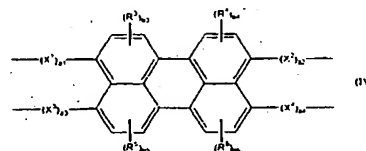
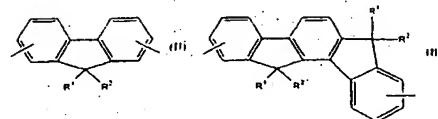
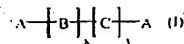
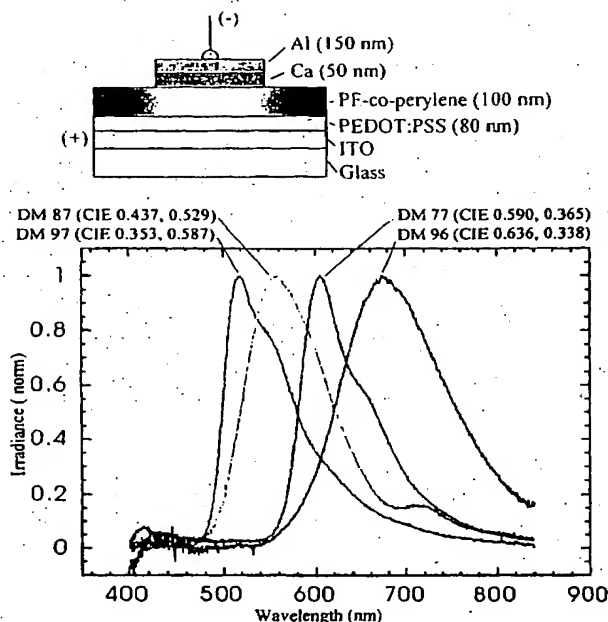
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9928981.1 9 December 1999 (09.12.1999) GB  
0018782.3 31 July 2000 (31.07.2000) GB(71) Applicants (for all designated States except US): CAM-  
BRIDGE DISPLAY TECHNOLOGY LIMITED  
[GB/GB]; Greenwich House, Madingley Rise, Madingley  
Road, Cambridge, Cambridgeshire CB3 0HJ (GB). MAX  
PLANCK INSTITUT FÜR POLYMERFORSCHUNG  
[DE/DE]; Ackermannweg 10, 55128 Mainz (DE).

(72) Inventors; and

(75) Inventors/Applicants (for US only): BECKER, Ste-  
fan [DE/DE]; Am Alten Weg 33, 55127 Mainz (DE).  
FRIEND, Richard [GB/GB]; Cambridge Display Tech-  
nology Limited, Greenwich House, Madingly Rise,  
Madingly Road, Cambridge, Cambridgeshire CB3 0HJ  
(GB). MÜLLEN, Klaus [DE/DE]; Geisbergstrasse 139  
(Kornhof), 50939 Köln (DE). MACKENZIE, Devin  
[GB/GB]; Cambridge Display Technology Limited, Green-  
wich House, Madingly Rise, Madingly Road, Cambridge,  
Cambridgeshire CB3 0HJ (GB). MARSITZKY, Dirk  
[DE/DE]; Theodor-Strom-Strasse 17, 67269 Grünstadt  
(DE). SETAYESH, Sepas [DE/DE]; Draiser Strasse 8,  
55128 Mainz (DE).(74) Agent: ANDREWS, Timothy, Stephen; Marks & Clerk,  
57-60 Lincoln's Inn Fields, London WC2A 3LS (GB).(81) Designated States (national): AE, AG, AL, AM, AT, AU,  
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(54) Title: FLUORENE-PERYLENE COPOLYMERS AND USES THEREOF



(57) Abstract: A statistical copolymer of formula (I) is provided wherein: A represents an end-capping unit; B is a moiety of formula (II) or (III), wherein each of R<sup>1</sup> and R<sup>2</sup> is hydrogen, alkyl, haloalkyl, alkoxy, alkoxyalkyl, aryl and aralkyl; C is a perylene-containing moiety of formula (IV), wherein each of a<sub>1</sub>, a<sub>2</sub>, a<sub>3</sub> and a<sub>4</sub> is 0 or 1, each of b<sub>3</sub>, b<sub>4</sub>, b<sub>5</sub> and b<sub>6</sub> is 0, 1 or 2, each of X<sup>1</sup>, X<sup>2</sup>, X<sup>3</sup> and X<sup>4</sup> is a single bond or a linking unit, and each of R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> is hydrogen, alkyl, haloalkyl, alkoxy, alkoxyalkyl, aryl, aryloxy or aralkyl; and the ratio x:y is from 80:20 to 99.9:0.1. A kit for the synthesis of the copolymers of the invention and electroluminescent devices incorporating said copolymers are also provided.

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**FLUORENE-PERYLENE COPOLYMERS AND USES THEREOF**

The present invention relates to novel fluorene-erylene copolymers. The copolymerisation of fluorene derivatives and perylene dyes provides a means of producing highly efficient luminescent polymers covering the visible spectrum. The statistical copolymers of the present invention show excellent film forming properties, are thermally very stable and can be easily solution-processed via spin-coating into LED sandwich structures which also form a part of the invention. The present invention also provides a kit for use in the production of the copolymers of the invention.

In recent years, there has been considerable interest in conjugated polymers. These are polymers which possess a delocalised pi-electron system along the polymer backbone. The delocalised pi-electron system confers semiconducting properties to the polymer and gives it the ability to support positive and negative charge carriers with high mobilities along the polymer chain. Thin films of these conjugated polymers can be used in the preparation of electroluminescent devices such as light-emitting devices. These devices have numerous advantages over devices prepared using conventional semiconducting materials, including the possibility of wide area displays, low dc working voltages and simplicity of manufacture. Devices of this type are described in, for example, WO-A-90/13148, US 5,512,654 and WO-A-95/06400.

The world market for displays based on organic and polymeric light-emitting materials has recently been estimated by Stanford Resources, Inc., to be \$ 200 million in the year 2002 with a strong growth rate which fuels the high industrial interest in this area (D.E. Mentley, "Flat Information Displays: Market and Technology Trends", 9<sup>th</sup> edition, 1998). Efficient and highly stable LED devices with low power consumption, which fulfill commercial requirements, have been prepared by a number of companies and academic research groups (see, for example, R.H. Friend et al., *Nature* 1999, 397, 12). As a result of this very fast development of polymer-based LEDs (PLEDs) compared to the development of inorganic LEDs (Sheats et al., *Science* 1996, 273, 884) the first effective monochromatic active- and passive-addressed matrix displays have been demonstrated to work and in 1999 PHILIPS announced the initiation of a manufacturing line for PLED display components (e.g. LEP backlights for the automotive and telecommunications industries).

At the moment, great efforts are dedicated to the realization of a full-colour, all plastic screen. The major challenges to achieve this goal are: (1) access to conjugated polymers emitting light of the three basic colours red, green and blue; and (2) the conjugated polymers must be easy to process and fabricate into full-colour display structures. PLED devices show great promise in meeting the first requirement, since manipulation of the emission colour can be achieved by changing the chemical structure of the conjugated polymers. However, while modulation of the chemical nature of conjugated polymers is often easy and inexpensive on the lab scale it can be an expensive and complicated process on the industrial scale. The second requirement of the easy processability and build-up of full-colour matrix devices raises the question of how to micro-pattern fine multicolour pixels and how to achieve full-colour emission. Inkjet printing and hybrid inkjet printing technology have recently attracted much interest for the patterning of PLED devices (see, for example, R.F. Service, *Science* 1998, 279, 1135; Wudl et al., *Appl. Phys. Lett.* 1998, 73, 2561; J. Bharathan, Y. Yang, *Appl. Phys. Lett.* 1998, 72, 2660; and T.R. Hebner, C.C. Wu, D. Marcy, M.L. Lu, J. Sturm, *Appl. Phys. Lett.* 1998, 72, 519).

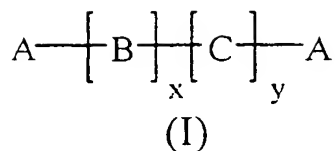
In order to contribute to the development of a full-colour display, we have sought a conjugated polymer exhibiting direct colour-tuning, good processability and the potential for inexpensive large-scale fabrication. The step-ladder polymer poly-2,7-fluorene (2,7-PF) has been the subject of much research into blue-light emitting polymers (see, for example, A. W. Grice, D. D. C. Bradley, M. T. Bernius, M. Inbasekaran, W. W. Wu, and E. P. Woo, *Appl. Phys. Lett.* 1998, 73, 629; and J. S. Kim, R. H. Friend, and F. Cacialli, *Appl. Phys. Lett.* 1999, 74, 3084) and has recently been made industrially available by DOW CHEMICALS. This class of conjugated polymers possesses excellent processability, endowed by the attachment of solubilizing groups at the remote C-9 position, without hampering the extended conjugation and therefore leading to high fluorescence quantum yields in the solid state (up to 79 %) (see, for example, Q. Pei, Y. Yang, *J. Am. Chem. Soc.* 1996, 118, 7416). Other benefits of 2,7-PF are its excellent thermal ( $T_d > 400^\circ\text{C}$ ) and chemical stability and its good film forming properties. The rigid nature of this polymer, however, enhances inter-chain aggregation leading to an undesired red-shift of the emission colour and a decreasing luminescence efficiency through excimer formation (see, for example, V. N. Bliznyuk, S. A. Carter, J. C. Scott, G. Klarnar, R. D. Miller, and D. C. Miller,

*Macromolecules*, 1999, 32, 361). Aggregation has been decreased through statistical copolymerization of 2,7-dibromofluorene with other halogenated monomers.

Several groups have shown that control of the emission colour in LEDs based on organic materials can be achieved by incorporating various dyes (see, for example, A. A. Shoustikov, Y. J. You and M. E. Thompson, "Electroluminescence Color Tuning by Dye Doping in Organic Light Emitting Diodes", *IEEE Journal of Selected Topics in Quantum Electronics* 1998, 4(1), 3-13; and B. Hu, N. Zhang and F.E. Karasz, *J. Appl. Phys.*, 1998, 83, 6002). These materials are marked by their rich variety of available bright colours. However, the small molecule chromophores can tend to crystallize or aggregate in PLED devices leading to degraded spectra and performance. Furthermore, molecular device processing using these materials lacks the processing simplicity and manufacturing advantages of solution-processable devices. The use of conjugated polymer/dye blends is another strategy to achieve a simple colour-tuning in LED devices (see, for example, B. Hu, N. Zhang, and F. E. Karasz, *J. Appl. Phys.*, 1998, 83, 6002). Problems associated with this approach include a lack of migration stability of the colourants under device operation, which may lead to poor efficiencies caused by a temperature-induced aggregation of the incorporated dye molecules.

A further approach recently disclosed by one group is the copolymerisation of 9,9-bis(2'-ethylhexyl)-2,7-dibromofluorene with brominated perylene and  $\alpha$ -cyanostilbene monomers (see J.-I. Lee, G. Klaerner and R.D. Miller, *Polymer Preprints* 1998, 1047; and J.-I. Lee, G. Klaerner, M.H. Davey and R.D. Miller, *Synthetic Materials* 1999, 102, 1087). These copolymers are said to address some of the problems noted above, including the fine-tuning of emissions and reduced excimer formation although PLEDs incorporating these copolymers may suffer reduced lifetime and the copolymers may also show unfavourable film-forming properties.

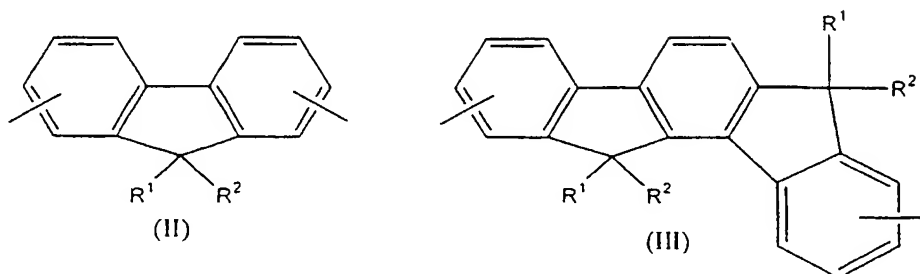
It is an object of the present invention to provide conjugated polymers exhibiting direct colour-tuning, good processability and the potential for inexpensive large-scale fabrication which do not exhibit the disadvantages noted above for the prior art polyfluorene-dye combinations. Thus, in a first aspect of the present invention there is provided a statistical copolymer of the following general formula (I):



wherein:

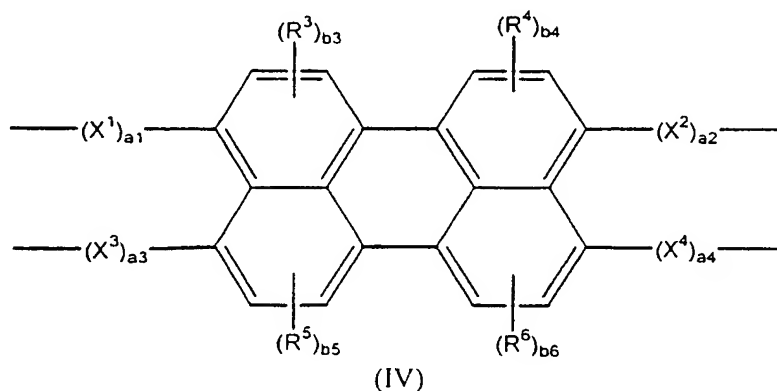
A represents an end-capping unit;

B represents at least one fluorene-containing moiety chosen from moieties of general formulae (II) and (III) below



wherein  $R^1$  and  $R^2$  are the same or different from each other and each is selected from the group consisting of hydrogen atoms, alkyl groups defined below, haloalkyl groups defined below, alkoxy groups defined below, alkoxyalkyl groups defined below, aryl groups defined below and aralkyl groups defined below;

C represents at least one perylene-containing moiety of general formula (IV)



wherein

$a_1$ ,  $a_2$ ,  $a_3$  and  $a_4$  are the same or different from each other and each is 0 or 1,

$b_3$ ,  $b_4$ ,  $b_5$  and  $b_6$  are the same or different from each other and each is 0, 1 or 2,

$X^1$ ,  $X^2$ ,  $X^3$  and  $X^4$  are the same or different from each other and each is a single bond or a linking unit, and

$R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  are the same or different from each other and each is selected from the group consisting of alkyl groups defined below, haloalkyl groups defined below, alkoxy groups defined below, alkoxyalkyl groups defined below, aryl groups defined below, aryloxy groups defined below and aralkyl groups defined below; and

the ratio x:y is from 80:20 to 99.9:0.1;

PROVIDED THAT, where A represents an unsubstituted fluorene group, each of b2 to b6 is 0, and either (i) each of a1 and a2 is 0, each of a3 and a4 is 1 and each of  $X^3$  and  $X^4$  is a single bond, or (ii) each of a1 and a4 is 0, each of a2 and a3 is 1 and each of  $X^2$  and  $X^3$  is a single bond, the ratio x:y is from 90:10 to 99.9:0.1;

the alkyl groups in the definitions of  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  above are straight or branched-chain alkyl groups having from 1 to 20 carbon atoms;

the haloalkyl groups in the definitions of  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  above are alkyl groups as defined above which are substituted by at least one halogen atom;

the alkoxy groups in the definitions of  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  above are straight or branched-chain alkoxy groups having from 1 to 20 carbon atoms,

the alkoxyalkyl groups in the definitions of  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  above and aryl groups below are alkyl groups as defined above which are substituted by at least one alkoxy group as defined above;

the aryl groups in the definitions of  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  above and aralkyl and aryloxy groups below are aromatic hydrocarbon groups having from 6 to 14 carbon atoms in one or more rings which may optionally be substituted by at least one substituent selected from the group consisting of nitro groups, cyano groups, amino groups, alkyl groups as defined above, haloalkyl groups as defined above, alkoxyalkyl groups as defined above, aryloxy groups as defined below and alkoxy groups as defined above;

the aryloxy groups in the definitions of  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  above are aryl groups as defined above which are bonded to any oxygen atom; and

the aralkyl groups in the definitions of  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  above are alkyl groups as defined above which are substituted by at least one aryl substituent as defined above.

The statistical fluorene-phenylene copolymers of general formula (I) of the present invention are highly efficient luminescent polymers covering the visible spectrum. They show excellent film forming properties, are thermally very stable and can be easily solution-processed

via spin-coating into LED sandwich structures. Furthermore, they exhibit greatly reduced excimer formation and inter-chain aggregation.

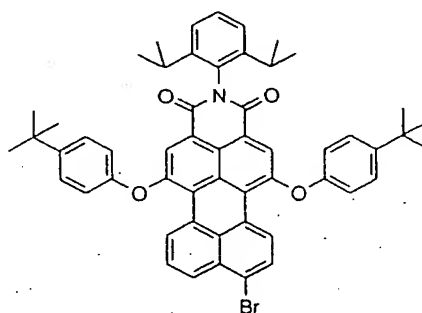
The perylene derivatives used in the preparation of the copolymers of the present invention exhibit several outstanding properties as they combine superior lightfastness and very long-term stability with high quantum yields of fluorescence, often close to 100 % in solution. Moreover perylene derivatives are remarkable in that a diversity of colours can be obtained by modifying the substituents attached to the aromatic perylene chromophore. Synthetic routes for this chemical modification of perylenes in high yields and on a large scale have been reported during the last few years (see, for example, P. Schlichting, U. Rohr, K. Müllen, *Liebigs Ann./Recueil* 1997, 395 –407; H. Quante, P. Schlichting, U. Rohr, Y. Geerts, K. Müllen, *Macromol. Chem. Phys.* 1996, 197, 4029-4044; and U. Rohr, P. Schlichting, A. Böhm, M. Groß, K. Meerholz, C. Bräuchle and K. Müllen, *Angewandte Chemie*, 1998, 110, 1463). This provides an elegant and highly effective strategy for the fine-tuning of the colour emission of fluorene-containing polymers.

In the copolymer of general formula (I) of the present invention, the ratio x:y (i.e. the molar ratio of the fluorene-containing moiety B to the perylene-containing moiety C) is from 80:20 to 99.9:0.1. Preferably, the ratio x:y is from 90:10 to 99.9:0.1 and most preferably from 94:6 to 99:1. Surprisingly, we have found that even where the amount of perylene in the copolymer of the present invention is very low, this is still sufficient to produce significant colour-tuning effects as well as providing a copolymer with many desirable characteristics such as excellent film forming properties, high thermal stability and easy solution-processability. Due to the extended lifetime and range of charges in a PLED relative to the lifetime of a photo-generated exciton, the efficiency of the colour-tuning is even greater in electroluminescent devices than optically-excited measurements of the emission of the copolymer used as the thin film in said device.

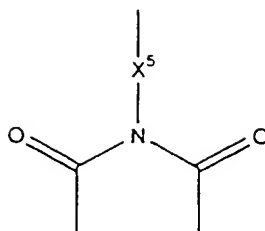
In the copolymer of general formula (I) of the present invention, the group A is an end-capping unit, i.e. it is a group which is introduced into the copolymer to prevent further chain growth. Preferably, the end-capping group A should be able to form a part of the delocalised pi-electron system along the polymer backbone. Typical examples of the end capping units include phenyl groups, fluorene groups and indenofluorene groups. One preferred option for the end-



capping units are dyes (e.g. perylene dyes) which can be introduced, for example, by the addition of monobrominated dyes. One example of such a monobrominated dye is (N-2,6-diisopropylphenyl)-1,6-bis(4-t-butylphenoxy)-9-bromoperylene-3,4-dicarboximide, the structure of which is shown below. The synthesis of this dye is described in H. Quante, K. Müllen, *Angew. Chemie* 1995, 107, 1487-1489 and in the PhD thesis of Quante, Johannes-Gutenberg-Universität 1994.



Where  $a_1$ ,  $a_2$ ,  $a_3$  or  $a_4$  is 0, then there is no linkage between the corresponding part of the perylene moiety and the adjacent moiety of formula (II), formula (III) or formula (IV). Where  $a_1$ ,  $a_2$ ,  $a_3$  or  $a_4$  is 1, the corresponding part of the perylene moiety is linked to the adjacent moiety of formula (II), formula (III) or formula (IV) through the corresponding group  $X^1$ ,  $X^2$ ,  $X^3$  or  $X^4$  which is chosen from the group consisting of single bonds and linking units. A linking unit is an organic moiety which acts as a bridging unit between the perylene moiety and the adjacent moiety of formula (II), formula (III) or formula (IV). Typical examples of the linking units include: arylene groups which are aromatic hydrocarbon groups having from 6 to 14 carbon atoms in one or more rings which may optionally be substituted by at least one substituent selected from the group consisting of nitro groups, cyano groups, amino groups, alkyl groups as defined above, haloalkyl groups as defined above, alkoxyalkyl groups as defined above, aryloxy groups as defined above and alkoxy groups as defined above; straight or branched-chain alkylene groups having from 1 to 6 carbon atoms; straight or branched-chain alkenylene groups having from 2 to 6 carbon atoms; and straight or branched-chain alkynylene groups having from 1 to 6 carbon atoms. Alternatively,  $X^1$  and  $X^2$  together and/or  $X^3$  and  $X^4$  together can represent a linking group of formula (V) below:



(V)

wherein  $X^5$  represents an arylene group which is an aromatic hydrocarbon group having from 6 to 14 carbon atoms in one or more rings which may optionally be substituted by at least one substituent selected from the group consisting of nitro groups, cyano groups, amino groups, alkyl groups as defined above, haloalkyl groups as defined above, alkoxyalkyl groups as defined above, aryloxy groups as defined above and alkoxy groups as defined above.

Preferably, either:

(i) one of  $a_1$  and  $a_2$  is 1 and the other is 0, and the corresponding group of formula  $X^1$  or  $X^2$  is a single bond, and one of  $a_3$  and  $a_4$  is 1 and the other is 0, and the corresponding group of formula  $X^3$  or  $X^4$  is a single bond; or

(ii) each of  $a_1$ ,  $a_2$ ,  $a_3$  and  $a_4$  is 1 and  $X^1$  and  $X^2$  together and  $X^3$  and  $X^4$  together each represent a group of formula (V) wherein  $X^5$  represents a phenylene group which may optionally be substituted by at least one substituent selected from the group consisting of alkyl groups as defined above, haloalkyl groups as defined above, alkoxyalkyl groups as defined above, aryloxy groups as defined above and alkoxy groups as defined above.

Within preferred option (ii),  $X^5$  is most preferably a phenylene group which is substituted by 1 or 2 straight or branched-chain alkyl groups having from 1 to 6 carbon atoms.

In the perylene-containing moiety of formula (IV), each of  $b_1$ ,  $b_2$ ,  $b_3$  and  $b_4$  represents 0, 1 or 2. Where any one of  $b_3$ ,  $b_4$ ,  $b_5$  and  $b_6$  is 2, then each of the corresponding substituents  $R^3$ ,  $R^4$ ,  $R^5$  or  $R^6$  may be the same or different from one another. Substituents  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  are preferably chosen from the group consisting of alkyl groups defined above, alkoxy groups defined above and optionally substituted aryloxy groups defined above; more preferably  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  are optionally substituted aryloxy groups defined above; still more preferably  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  are phenoxy groups which may optionally be substituted by at least one straight or

branched-chain alkyl group having from 1 to 8 carbon atoms or a straight or branched-chain alkoxy group having from 1 to 8 carbon atoms; and most preferably  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  are phenoxy groups which are substituted by a t-butyl group or a 1,1,3,3-tetramethylbutyl group.

In the perylene-containing moiety of formula (IV), preferred options include:

- (i) groups of formula (IV) wherein each of b3, b4, b5 and b6 is 0;
- (ii) groups of formula (IV) wherein one of b3 and b4 is 1 and the other is 0 and the corresponding group of formula  $R^3$  or  $R^4$  is a phenoxy group which is substituted by a straight or branched-chain alkyl group having from 1 to 8 carbon atoms, and one of b5 and b6 is 1 and the other is 0 and the corresponding group of formula  $R^5$  or  $R^6$  is a phenoxy group which is substituted by a straight or branched-chain alkyl group having from 1 to 8 carbon atoms;
- (iii) groups of formula (IV) wherein one of b3 and b4 is 1 and the other is 0 and the corresponding group of formula  $R^3$  or  $R^4$  is a phenoxy group which is substituted by a t-butyl group or a 1,1,3,3-tetramethylbutyl group, and one of b5 and b6 is 1 and the other is 0 and the corresponding group of formula  $R^5$  or  $R^6$  is a phenoxy group which is substituted by a t-butyl group or a 1,1,3,3-tetramethylbutyl group;
- (iv) groups of formula (IV) wherein each of b3, b4, b5 and b6 is 1 and each of  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  is the same or different and each is a phenoxy group which is substituted by a straight or branched-chain alkyl group having from 1 to 8 carbon atoms; and
- (v) groups of formula (IV) wherein each of b3, b4, b5 and b6 is 1 and each of  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  is a phenoxy group which is substituted by a t-butyl group or a 1,1,3,3-tetramethylbutyl group.

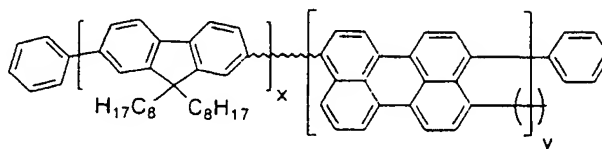
In the fluorene-containing moieties of formula (II) and formula (III),  $R^1$  and  $R^2$  are preferably the same or different from each other and each is a hydrogen atom or an alkyl group as defined above. More preferably, each of  $R^1$  and  $R^2$  is a straight or branched-chain alkyl group having from 1 to 10 carbon atoms; and most preferably each of  $R^1$  and  $R^2$  is the same and is a n-octyl group, a 2-ethylhexyl group or a 1,1,3,3-tetramethyl group.

B can represent one moiety of formula (II) or formula (III) and C can represent one moiety of formula (IV) in a given copolymer of formula (I) of the present invention or B can

represent two or more different moieties of formula (II) or formula (III) and/or C can represent two or more different moieties of formula (IV) in the same copolymer.

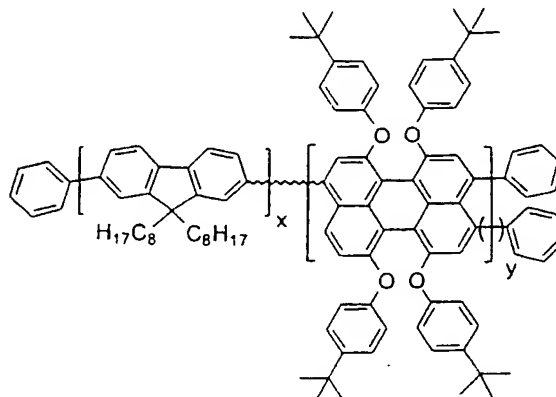
Preferred copolymers of formula (I) of the present invention include the following:

(i)



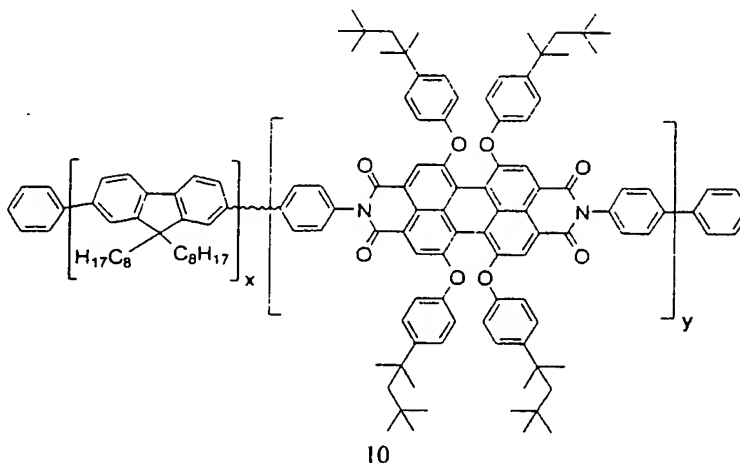
wherein the ratio x:y is preferably from 95:5 to 99.9:0.1, and particularly preferably is 97:3;

(ii)



wherein the ratio x:y is preferably from 95:5 to 99.9:0.1, and particularly preferably is 95:5;

(iii)

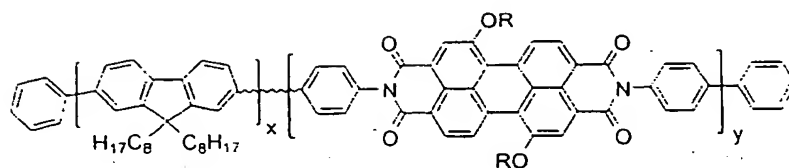


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**SUBSTITUTE SHEET (RULE 26)**

wherein the ratio  $x:y$  is preferably from 95:5 to 99.9:0.1, and particularly preferably is 99:1:

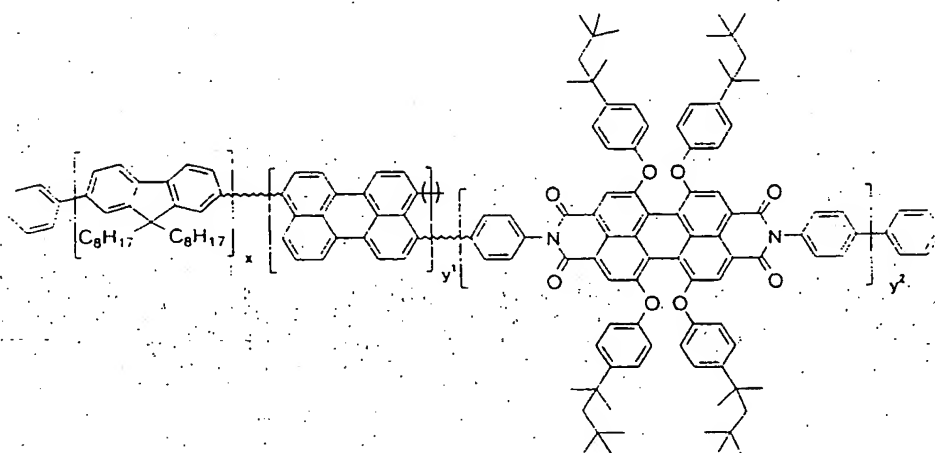
(iv)



wherein R =

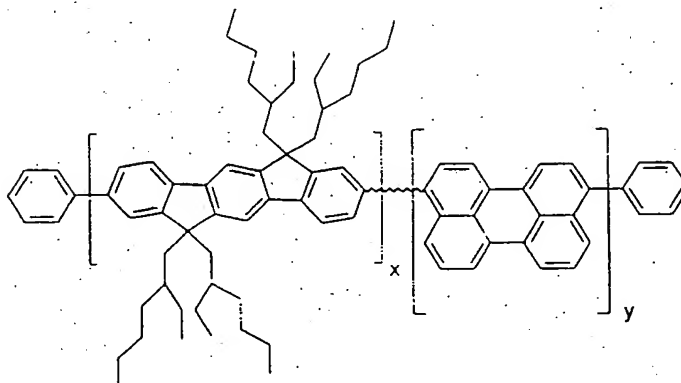
wherein the ratio  $x:y$  is preferably from 95:5 to 99.9:0.1, and particularly preferably is 95:5:

(v)



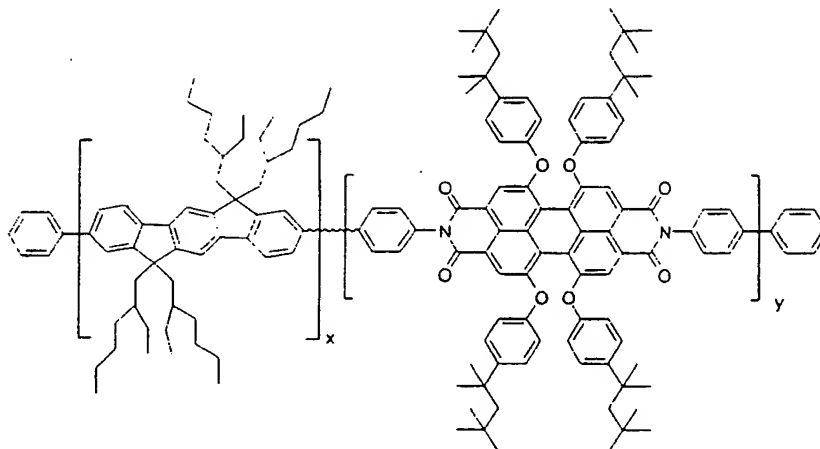
wherein the ratio  $x:y^1:y^2$  is preferably from 94:3:3 to 99.8:0.1:0.1, and particularly preferably is 94:3:3:

(vi)



wherein the ratio  $x:y$  is preferably from 95:5 to 99.9:0.1, and particularly preferably is 99:1; and

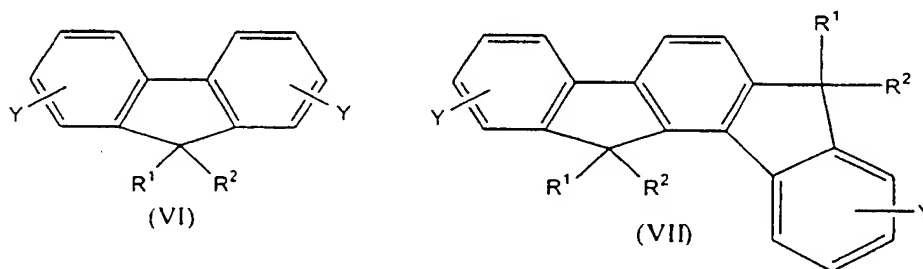
(vii)



wherein the ratio  $x:y$  is preferably from 95:5 to 99.9:0.1, and particularly preferably is 99:1.

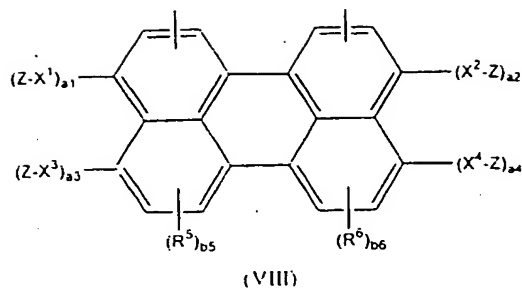
In a further embodiment of the present invention there is provided a kit for the synthesis of the copolymer of formula (I) of the present invention comprising:

(i) at least one fluorene-containing monomer of general formula (VI) or (VII)



wherein  $R^1$  and  $R^2$  are as defined above and  $Y$  is a group capable of leaving as a nucleophile; and

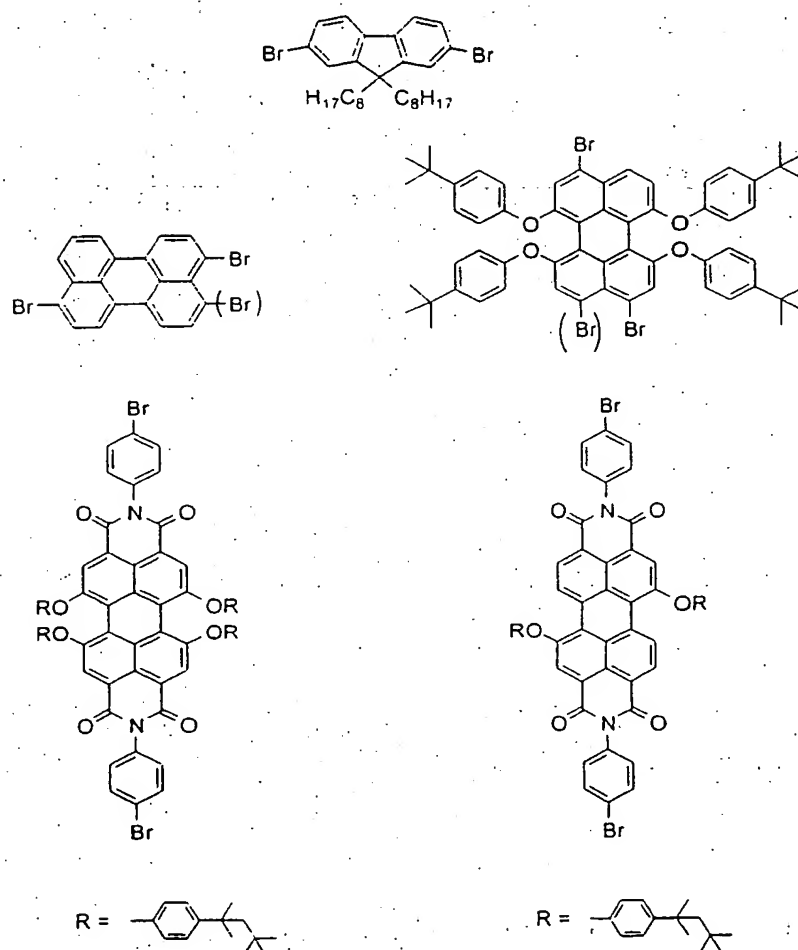
(ii) at least one perylene-containing monomer of general formula (VIII)



wherein a1, a2, a3, a4, b3, b4, b5, b6, X<sup>1</sup>, X<sup>2</sup>, X<sup>3</sup>, X<sup>4</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> are as defined above and Z is a group capable of leaving as a nucleophile.

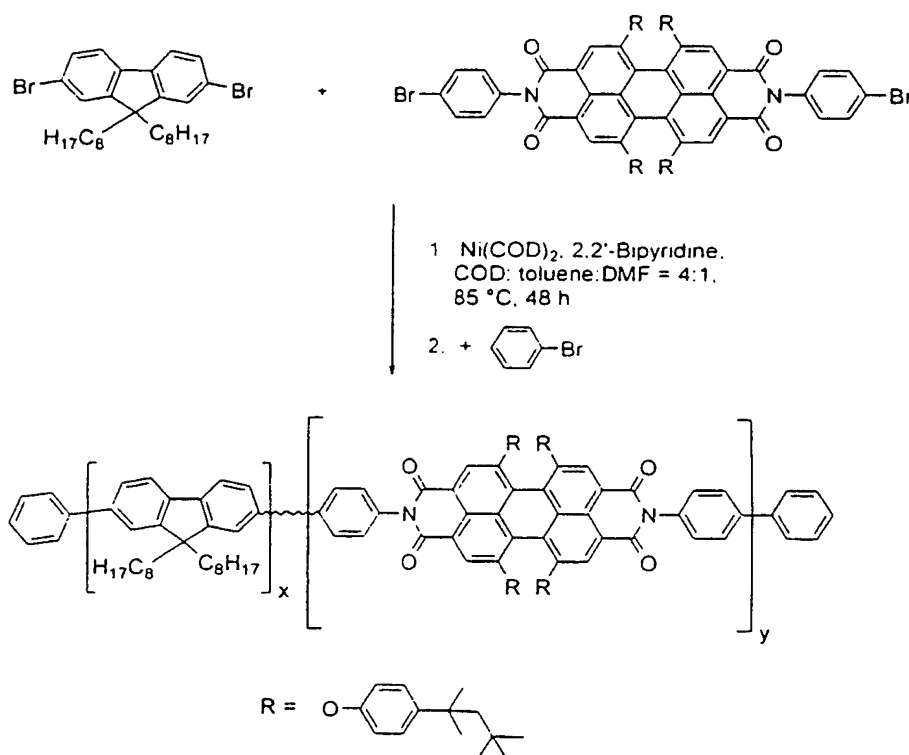
Y and Z are groups which are capable of leaving as a nucleophile and typical examples include halogen atoms, triflate groups and mesylate groups. Preferably, each of Y and Z is a bromine atom.

A typical kit of the present invention might include the following monomers:



The copolymerization of the monomers of formulae (VI) and/or (VII) above with the monomers of formulae (VIII) above can be easily performed according to a Yamamoto-coupling protocol [see, for example, T. Yamamoto, "Electrically Conducting And Thermally Stable  $\pi$ -Conjugated Poly(arylene)s Prepared by Organometallic Processes", *Progress in Polymer Science* 1993, 17, 1153-1205]. The removal of the residual end-groups of formulae Y and Z above is important as it has been shown that these end-groups, particularly bromine end-groups, are detrimental to the performance of PLED devices incorporating such polymers. These residual end-groups are removed by the introduction of the end-capping groups A, as defined above. The copolymers are obtained in fair to good yields (57-78 %), exhibit high molecular weight ( $M_n$  = 30 000 g/mol – 70 000 g/mol) and excellent film forming properties and are soluble in common organic solvents. Thermogravimetric analysis (TGA) measurements reveal the high thermal stability of the copolymers of the present invention up to 390 °C.

A typical copolymerisation procedure for the production of a copolymer of formula (I) according to the present invention using the Yamamoto-coupling protocol is shown below, in which COD represents cyclooctadiene:





Other polymerisation techniques well-known in the art can also be used in the synthesis of copolymers according to the present invention. e.g. Suzuki polymerisation (see Suzuki et al., *Synth. Comm.*, 1981, 11, 513).

Using different perylene dyes, copolymers having bright green and red emission have been realized by internal colour conversion of the polyfluorene. Luminescence of different colours is generated by an internal excitation energy transfer (Förster-type) from the blue emitting polyfluorene to green or red emitting perylene derivatives. The strategy of copolymerizing the perylene dyes and the fluorenes suppresses crystallization and aggregation of dyes which occurred in the prior art where they were physically dissolved in the fluorene polymer.

The intramolecular energy transfer in the copolymers of the present invention is very efficient in the solid-state, so that only a few percent of a perylene dye is necessary to alter the blue polyfluorene emission in such a way that green or red luminescence is generated. Absolute photoluminescence efficiencies, measured from thin films of the copolymers of the present invention spun on quartz substrates following de Mello et al. (see J. C. de Mello, H. F. Wittman, and R. H. Friend, *Adv. Mater.*, 1997, 9, 230) have been found to range from approximately 33% to approximately 51% with peak emissions in the range 545 nm to 610 nm, as compared to approximately 56% for the polyfluorene homopolymer with vibronically-structured emission centred near 465 nm.

Electroluminescent devices such as thin-film LED structures incorporating the copolymers of formula (I) of the present invention can be fabricated, and these devices also form a part of the present invention. A typical thin-film LED structure of this type comprises O<sub>2</sub> plasma-treated ITO-coated glass, a poly(styrene sulfonate)-doped poly(3,4-ethylene dioxythiophene) (PEDOT:PSS) hole injection layer, a thin film of a copolymer of formula (I) of the present invention, and a Ca-Al cathode. The PEDOT:PSS films (typically approximately 70 nm in thickness) can be spun from a filtered H<sub>2</sub>O solution before heating to 100°C under N<sub>2</sub> for 30 minutes. Spin-coating can also be used to deposit the emissive copolymer films of the present invention (typically approximately 100 nm in thickness) from xylene solutions in a nitrogen-filled glove box. The Ca cathode (typically approximately 500 Å in thickness) and Al protective layers (typically approximately 1500 Å in thickness) can be deposited by thermal

evaporation in a vacuum (e.g. base pressure approximately  $5 \times 10^{-6}$  mbar) patterned by a shadow mask.

Electrically-stimulated emission spanning the visible range has been observed for LEDs incorporating copolymers of formula (I) according to the present invention produced using the above process. It should be noted that the devices produced so far are a first demonstration of the colour-tuning capability of the fluorene-peryene copolymers of the present invention and have not yet been optimized. It has been shown that careful optimization of anode layer treatment and thickness as well as emitter layer thickness for a particular polymer can dramatically improve the device performance, including such parameters as turn-on voltage and efficiency (see, for example, P. K. H. Ho, D. S. Thomas, R. Friend, and N. Tessler, *Science* 1999, 285, 234; and P. K. H. Ho, M. Granstrom, R. H. Friend, and N. C. Greenham, *Adv. Mater.* 1998, 10, 769). External quantum efficiencies ranging from 0.6% in the green to 0.3% in the red achieved for LEDs based on the fluorene-peryene copolymers of the present invention demonstrate the potential for efficient emission over the entire spectrum. Electroluminescence lifetime experiments have shown that the copolymers of the present invention can be significantly more stable than the corresponding polyfluorene/dye blends of the prior art in terms of electrical characteristics and emission spectra.

The present invention may be further understood by consideration of the following embodiments of the present invention, with reference to the following drawings in which:

Figure 1 shows a schematic representation of a PLED device incorporating a copolymer according to the present invention:

Figure 2 shows the electroluminescence spectra for PLED devices incorporating a number of copolymers of the present invention; and

Figure 3 shows plots of current and luminescence versus voltage for a copolymer of the present invention.

In the following, we first describe the synthesis of a number of copolymers according to the present invention. We then describe the synthesis of various perylene dyes used in the synthesis of the preceding copolymers. Finally, we describe some experiments conducted to determine various properties of the copolymers that had been prepared.

## Synthesis of Fluorene-Perylene Statistical Copolymers

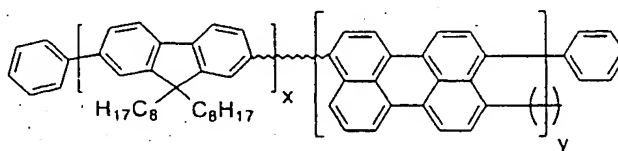
### General Procedure for the Preparation of the Copolymers

In a glove box (pure nitrogen atmosphere with strict exclusion of moisture and oxygen) 303 mg (1.1 mmol) of bis(cyclooctadiene)nickel(0), 172 mg (1.1 mmol) of 2,2'-bipyridine, and 0.14 ml (1.1 mmol) of cyclooctadiene were dissolved in 10 ml of dry toluene and 4 ml of dry DMF in a Schlenk flask. The flask was closed with a septum and the deep blue catalyst solution was activated by heating to 80 °C for approximately 20 minutes. At the end of this time a solution of 300 mg (0.55 mmol) of 2,7-dibromo-9,9-di-n-octylfluorene and 0.0275 mmol (for a 5 % dye content) of a bisbrominated perylene dye in 20 ml dry toluene was added with a syringe. The mixture was heated to 80 °C and stirred for 24 hours. At the end of this time, 3 mmol of bromobenzene were added with a syringe to end-cap the copolymers and then heating and stirring was continued for a further 2 hours.

After cooling to room temperature the reaction mixture was diluted with 100 ml toluene, washed first with diluted aqueous HCl and then with a solution of 5 % EDTA in 10 % aqueous ammonia. The phases were separated, the organic phase was concentrated under reduced pressure and the product was precipitated by slowly adding the solution to 400 ml of a mixture consisting of 1 part methanol, 1 part acetone and 0.2 parts of 2M aqueous HCl. The product was filtered, washed several times with acetone and methanol and vacuum dried.

### Example 1

#### Polv-[2,7-(9,9-di-n-octylfluorene)]-co-[3,9(10)-perylene] (DM97)



Using the general procedure described above, 2,7-dibromo-9,9-di-n-octylfluorene was copolymerised with 3 mol. % of 3,9-dibromoperylene and 3,10-dibromoperylene (a mixture of the two isomers) to give the title copolymer in which the ratio x:y is 97:3.

Product: yellow solid (yield 69 %).

$^1\text{H-NMR}$  (300 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  (ppm) = 0.80 (t, 7.8 Hz, 6 H), 0.90-1.21 (m, 12 H), 1.86-2.19 (m, 4 H), 7.61-7.88 (m, 6H + 10 H perylene).

$^{13}\text{C-NMR}$  (125 MHz, 353 K,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  (ppm) = 14.0, 22.6, 24.1, 29.1, 29.2, 30.0, 31.7, 40.1, 55.3, 120.0, 121.7, 126.1, 132.5 (w), 140.1, 140.5, 152.0.

GPC (THF, PS-Standard, UV-detection):  $M_n = 47\,900$  g/mol ( $D = 4.08$ , UV 390 nm)

$M_n = 48\,700$  g/mol ( $D = 4.00$ , UV 470 nm).

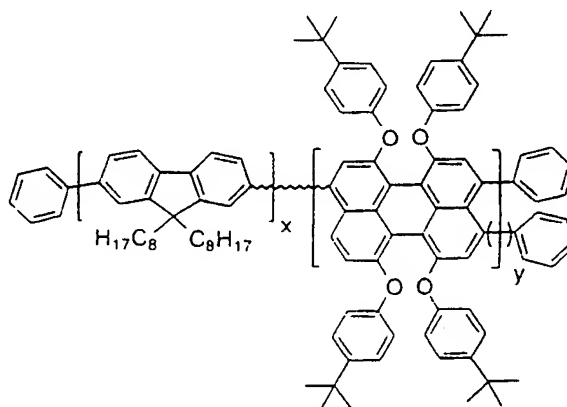
IR (KBr):  $\nu$  [ $\text{cm}^{-1}$ ] = 669, 757, 885, 999, 1253, 1402, 1457, 1636, 2852, 2925, 3022.

UV ( $\epsilon$ ): 387 nm (698 500 l/mol\*cm), 428 nm (21 300 l/mol\*cm) solution in (THF)  
410 nm, 438 nm (solid film).

Fluorescence ( $\lambda_{\text{exc}} = 370$  nm, film on silica): 443 nm, 473 nm, 525 nm.

### Example 2

Polv-[2,7-(9,9-di-n-octylfluorene)]-co-[3,9(10)-[1,6,7,12-tetra(4-t-butylphenoxy)perylene]]  
[DM87]



Using the general procedure described above, 2,7-dibromo-9,9-di-n-octylfluorene was copolymerised with 5 mol. % of 3,9-dibromo-1,6,7,12-tetra(4-tert.-butylphenoxy)perylene and 3,10-dibromo-1,6,7,12-tetra(4-tert.-butylphenoxy)perylene (a mixture of the isomers) to give the title copolymer in which the ratio x:y is 95:5.

Product: yellow-green solid (yield: 62 %).

$^1\text{H-NMR}$  (300 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  (ppm) = 0.52- 1.02 (m, 30 H), 1.25 (s.b, tert.butyl-perylene-H), 1.86-2.19 (m, 4 H), 6.82 (b, AA'BB'-phenoxy-H), 7.13 (b, AA'BB'-phenoxy-H), 7.65-7.92 (m, 6H fluorene + 6 H perylene).

$^{13}\text{C-NMR}$  (125 MHz, 353 K,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  (ppm) = 14.2, 22.1, 24.3, 29.5, 29.7, 30.4, 31.3, 40.7, 55.2, 121.1, 121.9, 127.0, 140.6, 141.1, 152.4.

GPC (THF, PS-standard, UV-detection):  $M_n = 32\,300$  g/mol ( $D = 4.89$ , UV 360 nm)

$M_n = 37\,400$  g/mol ( $D = 4.37$ , UV 450 nm).

IR (KBr):  $\nu$  [ $\text{cm}^{-1}$ ] = 675, 735, 894, 989, 1248, 1413, 1451, 1630, 2851, 2924, 3020.

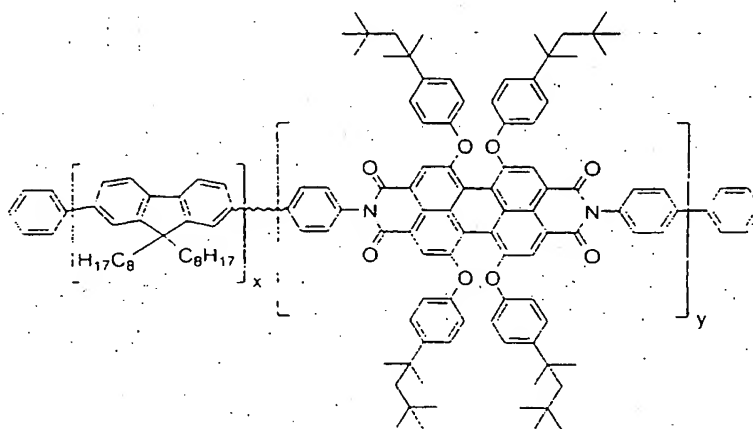
UV : 389 nm (617 200 l/mol\*cm), 474 nm (7600 l/mol\*cm) (solution in THF)

400 nm, 494 nm (solid film).

Fluorescence ( $\lambda_{\text{exc}} = 370$  nm, solid film): 421 nm, 443 nm, 540 nm.

### Example 3

Polv-[2,7-(9,9-di-n-octylfluorene)]-co-[4,4'-(N,N'-diphenyl)-[1,6,7,12-tetra[4-(1,1,3,3-tetramethylbutyl)phenoxy]perylene]-3,4:9,10-tetracarboxdiimide] [DM77]



Using the general procedure described above, 2,7-dibromo-9,9-di-n-octylfluorene was copolymerised with 1 mol. % of N,N'-[di-(4-bromophenyl)]-[1,6,7,12-tetra[4-(1,1,3,3-tetramethylbutyl)-phenoxy]perylene]-3,4:9,10-tetracarboxdiimide to give the title copolymer in which the ratio x:y is 99:1.

Product: red solid (yield 76 %)

$^1\text{H-NMR}$  (300 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  (ppm) = 0.75 (b, 6 H + 9 H tert.butyl-perylene-H), 0.92-1.19 (m, 12 H), 1.29 (s, 6 H alkyl-phenoxy-H), 1.66 (s, 2 H alkyl-phenoxy-H), 1.89-2.15 (m, 4 H octyl- $\alpha$ - $\text{CH}_2$ ), 6.87 (b, 8 H, arom. phenoxy-H), 7.22 (b, 8 H, arom. phenoxy-H) 7.49-7.90 (m, 6H), 8.14 (arom. perylene-H).

$^{13}\text{C-NMR}$  (125 MHz, 353 K,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  (ppm) = 14.1, 22.7, 24.3, 29.3, 30.2, 31.6, 31.9, 32.1, 55.6, 120.1, 122.0, 129.2 (w) 126.3, 140.3, 140.8, 152.2.

GPC (THF, PS-standard, UV-detection):  $M_n = 75\,200$  g/mol ( $D = 6.26$ , UV 360 nm)

$M_n = 71\,500$  g/mol ( $D = 6.15$ , UV 580 nm).

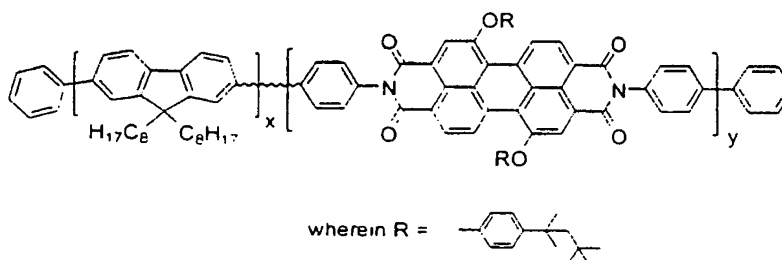
IR (KBr):  $\nu$  [ $\text{cm}^{-1}$ ] = 728, 748, 824, 881, 999, 1069, 1254, 1371, 1412, 1452, 1516, 1591, 1677, 1705, 1871, 2857, 2915, 2959, 3008, 3065.

UV: 386 nm (654 500 l/mol\*cm), 582 nm (8 300 l/mol\*cm) solution in ( $\text{CH}_2\text{Cl}_2$ )  
398 nm, 433 nm, 541 nm, 579 nm (solid film).

Fluorescence ( $\lambda_{\text{exc}} = 370$  nm, solid film): 433 nm, 440 nm, 467 nm, 623 nm.

#### Example 4

**Polv-[2,7-(9,9-di-n-octylfluorene)]-co-[4,4'-(N,N'-diphenyl)-[1,7-di[4-(1,1,3,3-tetramethyl-butyl)phenoxy]perylene]-3,4:9,10-tetracarboxdiimide] [DM96]**



Using the general procedure described above, 2,7-dibromo-9,9-di-n-octylfluorene was copolymerised with 5 mol. % of N,N'-[di-(4-bromophenyl)]-1,7-di[4-(1,1,3,3-tetramethylbutyl-phenoxy)]perylene-3,4:9,10-tetracarboxdiimide to give the title copolymer in which the ratio x:y is 95:5.

Product: dark red solid(yield 64 %)

$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 0.80 (b, 6 H + 9 H tert.butyl-perylene-H). 0.94-1.28 (m, 12 H), 1.31 (s, 6 H alkyl-phenoxy-H), 1.68 (s, 2 H alkyl-phenoxy-H), 1.89-2.15 (m, 4 H octyl- $\alpha$ - $\text{CH}_2$ ), 7.82-7.92 (m, 6H), 8.81 (s, arom. perylene-H), 9.71 (b, imidphenyl-H).

$^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 14.3, 22.5, 24.8, 29.6, 30.5, 31.4, 31.5, 32.3, 55.4, 120.0, 122.7, 126.5, 140.2, 140.5, 152.0.

GPC (THF, PS-standard, UV-detection):  $M_n = 63\,500$  g/mol ( $D = 3.58$ , UV 390 nm)

$M_n = 55\,400$  g/mol ( $D = 3.84$ , UV 500 nm).

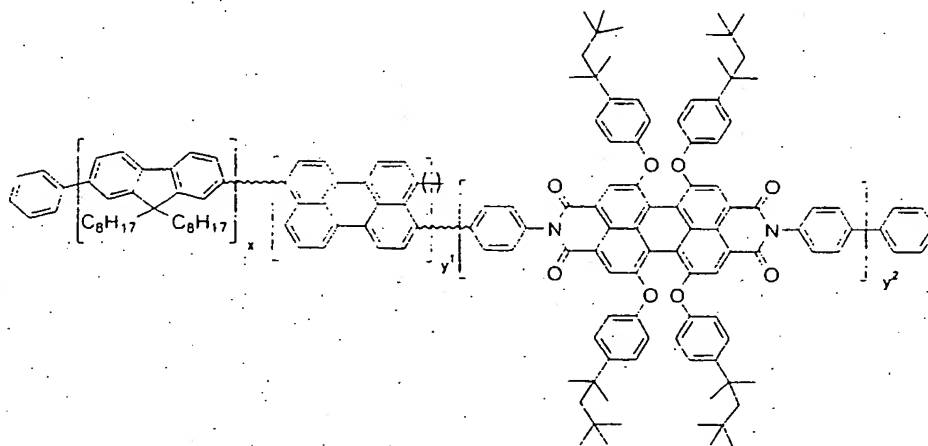
IR (KBr):  $\nu$  [ $\text{cm}^{-1}$ ] = 722, 755, 815, 881, 988, 1073, 1254, 1371, 1416, 1459, 1512, 1599, 1674, 1716, 1865, 2878, 2935, 2947, 3015, 3069.

UV (solid film): 389 nm (675 400 l/mol\*cm), 772 nm (13 300 l/mol\*cm) solution in (THF)  
407 nm, 514 nm, 553 nm (solid film).

Fluorescence ( $\lambda_{\text{exc}} = 350$  nm, solid film): 425 nm, 442 nm, 643 nm.

### Example 5

Polv-[2,7-(9,9-di-n-octylfluorene)]-co-[3,9(10)-perylene]-co-[4,4'-(N,N'-diphenyl)-[1,6,7,12-tetra[4-(1,1,3,3-tetramethylbutyl)phenoxy]perylene]-3,4:9,10-tetracarboxdiimide]



Using the general procedure described above, 2,7-dibromo-9,9-di-n-octylfluorene was copolymerised with 3 mol.% of N,N'-[di-(4-bromophenyl)]-[1,6,7,12-tetra[4-(1,1,3,3-tetramethylbutyl)phenoxy]perylene]-3,4:9,10-tetracarboxdiimide and 3 mol.% of a mixture of the isomers 3,9-dibromoperylene and 3,10-dibromoperylene to give the title copolymer in which the ratio  $x:y^1:y^2$  is 94:3:3.

Product: brown solid (yield: 67 %)

$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 0.75 (b, 6 H + 9 H tert.-butyl-perylene-H), 0.91-1.23 (m, 12 H), 1.31 (s, alkyl-phenoxy-H), 1.68 (s, alkyl-phenoxy-H), 1.89-2.15 (m, 4 H Octyl- $\alpha$ - $\text{CH}_2$ ), 7.75-7.92 (m, 6H + 8 dibromoperylene-H), 8.78 (s, arom. tetraphenoxyperylenediimide-H), 9.70 (b, imidphenyl-H).

$^{13}\text{C-NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 14.2, 22.4, 24.5, 29.3, 30.4, 31.6, 31.3, 32.1, 55.7, 120.1, 122.5, 126.2, 140.1, 140.7, 151.9.

GPC (THF, PS-standard, UV-detection):  $M_n = 46\,600$  g/mol ( $D = 7.68$ , UV 390 nm)

$M_n = 39\,100$  g/mol ( $D = 8.98$ , UV 470 nm).

IR (KBr):  $\nu$  [ $\text{cm}^{-1}$ ] = 715, 741, 836, 876, 989, 1057, 1254, 1378, 1418, 1459, 1519, 1599, 1667, 1721, 1869, 2865, 2910, 2955, 3010, 3062.

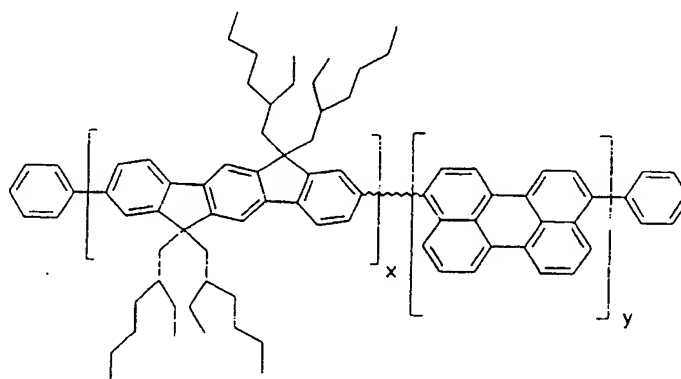
UV (solid film): 404 nm, 458 nm, 492 nm, 527 nm, 564 nm.

Fluorescence ( $\lambda_{\text{exc.}} = 350$  nm, solid film): 425 nm, 441 nm, 466 nm, 622 nm.

TGA measurements were performed for the copolymers of Examples 1 to 5. The result was that all the copolymers are thermally very stable (decomposition starts at 440 °C)

### Example 6

#### Polv-[2,8-[6,6,12,12-tetra(2-ethylhexyl)indenofluorene]]-co-[3,9(10)-perylene]



$x = 99$ ;  $y = 1$



Using the general procedure described above, 2,8-dibromo-[6,6,12,12-tetra(2-ethylhexyl)]indeno[1,2-b]fluorene was copolymerised with 1 mol. % of a mixture of the isomers 3,9-dibromoperylene and 3,10-dibromoperylene to give the title copolymer in which the ratio x:y is 99:1.

Product: Yellow solid

$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.82 (s, 2 H), 7.75 (s, 2H), 7.67 (s, 4 H), 2.21 (m, 8 H), 0.9 (m, 30 H).

$^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 151.21, 150.25, 140.81, 140.21, 126.11, 122.67, 119.28, 115.10, 54.69, 44.33, 34.89, 34.08, 28.54, 28.20, 26.95, 22.77, 13.97, 13.97, 10.13.

GPC (toluene, polystyrene standard):  $M_n = 33000$ ;  $M_w = 100000$ ;  $D = 3.0$

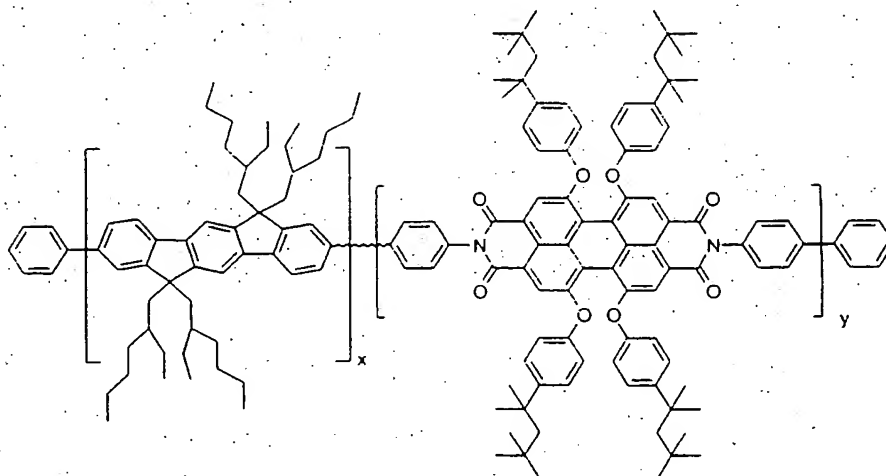
Absorbance max: 417 nm (Chloroform solution)

Fluorescence max: 427, 252, 492 nm (Chloroform solution; excitation: 380 nm)

Fluorescence max: 507 nm (solid film; excitation: 380 nm)

### Example 7

Polv-[2,8-[6,6,12,12-tetra(2-ethylhexyl)]indeno[1,2-b]fluorene]-co-[4,4'-(N,N'-diphenyl)-[1,6,7,12-tetra[4-(1,1,3,3-tetramethylbutyl)phenoxy]perylene]-3,4:9,10-tetracarboxdiimide]



Using the general procedure described above, 2,8-dibromo-[6,6,12,12-tetra(2-ethylhexyl)]indeno[1,2-b]fluorene was copolymerised with 1 mol. % of N,N'-[di-(4-bromophenyl)]-

[1.6.7.12-tetra[4-(1,1,3,3-tetramethylbutyl)phenoxy]perylene]-3,4:9,10-tetracarboxdiimide to give the title copolymer in which the ratio x:y is 99:1.

Product: Red solid

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.24 (arom. perylene-H), 7.80 (s, 2 H), 7.72 (s, 2H), 7.77 (s, 4 H), 7.21 (8 H, arom. phenoxy-H), 6.77 (8 H, arom. phenoxy-H), 2.21 (s, 8 H), 1.65 (s, 2 H, alkyl-phenoxy-H), 1.26 (s, 6 H, alkyl-phenoxy-H); 1.0 (m, 30 H, 9 H tert-butyl-perylene-H).

<sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) = 151.41, 150.15, 140.76, 140.18, 126.00, 122.80, 119.33, 114.99, 54.65, 44.43, 34.74, 34.01, 28.49, 28.12, 26.95, 22.83, 14.13, 14.02, 10.22.

GPC: (toluene, polystyrene standard) Mn = 12000, Mw = 42000; D = 3.5.

Absorbance max: 422 nm (Chloroform solution).

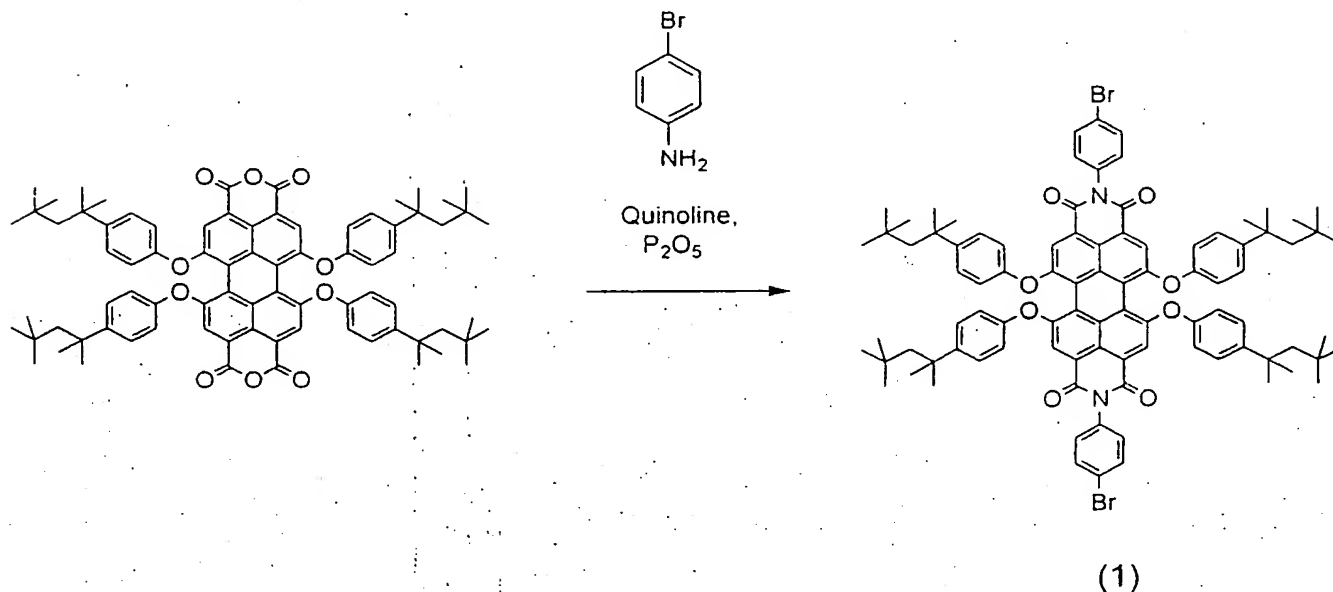
Fluorescence max: 429, 252 nm (Chloroform solution: excitation: 380 nm).

Fluorescence max. 602, 434, 456 nm (solid film: excitation: 380 nm).

#### **Synthesis of Perylene Dyes Used in the Above Synthesis of Light Emitting Conjugated Polymers**

The syntheses of 3,9(10)-dibromoperylene used in Examples 1, 5 and 6 above and 3,9(10)-1,6,7,12-tetra(4-t-butylphenoxy) perylene used in Example 2 above are published in P. Schlichting, U. Rohr, K. Müllen, *Liebigs Ann./Recueil* 1997, 395 —407 and H. Quante, P. Schlichting, U. Rohr, Y. Geerts, K. Müllen, *Macromol. Chem. Phys.* 1996, 197, 4029-4044 respectively.

The syntheses of 4,4'-[N,N'-di-(4-bromophenyl)]-[1.6.7,12-tetra[4-(1,1,3,3-tetramethylbutyl)-phenoxy]perylene]-3,4:9,10-tetracarboxdiimide used in Examples 3, 5 and 7 above and N,N'-[di-(4-bromophenyl)]-1,7-di[4-(1,1,3,3-tetramethylbutyl)phenoxy]perylene-3,4:9,10-tetracarboxdiimide used in Example 4 above is described in Preparative Examples 1 and 2 below.

Preparative Example 14,4'-[N,N'-di-(4-bromophenyl)]-[1,6,7,12-tetra[4-(1,1,3,3-tetramethylbutyl)phenoxy]-  
perylene]-3,4:9,10-tetracarboxdiimide (1)

The synthesis of the starting material 1,6,7,12-tetra[4-(1,1,3,3-tetramethylbutyl)phenoxy]perylene]-3,4:9,10-tetracarboxdianhydride is described in H. Quante, P. Schlichting, U. Rohr, Y. Geerts, K. Müllen, *Macromol. Chem. Phys.* 1996, 197, 4029-4044. In a single-necked flask (250 mL) 3.63 g (3 mmol) of 1,6,7,12-tetra[4-(1,1,3,3-tetramethylbutyl)phenoxy]perylene]-3,4:9,10-tetracarboxdianhydride were finely suspended in 100 mL anhydrous quinoline. Then, 7.09 g (40 mmol) of 4-bromoaniline and 0.5 g of phosphorous pentoxide were added and the mixture heated at 160 °C under an argon atmosphere for 8 hours. After cooling to room temperature the mixture was poured into 500 mL of 10 % hydrochloric acid. The precipitate was filtered, washed extensively with a mixture of methanol and water (50/50, v/v) and dried under vacuum at 100 °C. The crude product was purified by column chromatography on silica gel using a mixture of dichloromethane and hexane (70/30, v/v) as the eluent. 4.10 g (90 % yield) of the title compound was produced as a dark red solid.

m.p. = 334 °C

MS (8 kV, FD): m/z = 1514.6 (100 %) [M<sup>+</sup>] (calculated: 1514.55)

$^1\text{H-NMR}$  (300 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 25 °C):  $\delta$  (ppm) = 8.13 (s, 4 H.), 7.59 (d, 4 H,  $^3\text{J}(\text{H,H}) = 8.52$  Hz), 7.24 (d, 8 H,  $^3\text{J}(\text{H,H}) = 8.53$  Hz), 7.09 (d, 4 H,  $^3\text{J}(\text{H,H}) = 8.52$  Hz), 6.87 (d, 8 H,  $^3\text{J}(\text{H,H}) = 8.53$  Hz), 1.68 (s, 8 H), 1.32 (s, 24 H), 0.75 (s, 36 H).

$^{13}\text{C-NMR}$  (J-modulated spinecho, 75 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 25 °C):  $\delta$  (ppm) = 163.40 (C=O), 156.67 (arom. Cq), 152.76 (arom. Cq), 147.47 (arom. Cq), 134.58 (arom. Cq), 133.32 (arom. Cq), 132.73 (arom. CH), 130.68 (arom. CH), 127.92 (arom. CH), 122.87 (arom. Cq), 122.73 (arom. Cq), 120.81 (arom. Cq), 119.99 (arom. CH), 119.81 (arom. CH), 57.39 (aliph. Cq), 38.65 (aliph. Cq), 32.53 (aliph.  $\text{CH}_2$ ), 32.12 (aliph.  $\text{CH}_3$ ), 31.65 (aliph.  $\text{CH}_3$ ).

UV/VIS (chloroform solution):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 453 nm ( $14294 \text{ L mol}^{-1} \text{ cm}^{-1}$ ), 548.5 nm ( $23959 \text{ L mol}^{-1} \text{ cm}^{-1}$ ), 591.5 nm ( $40400 \text{ L mol}^{-1} \text{ cm}^{-1}$ ).

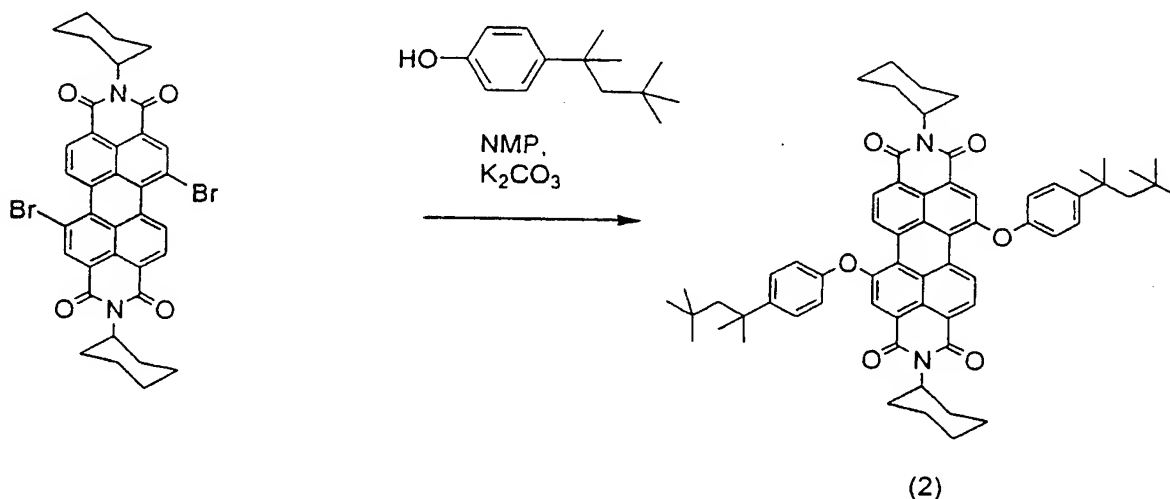
Fluorescence (chloroform solution, excitation: 550 nm):  $\lambda_{\text{max}} = 626 \text{ nm}$ .

Elemental analysis found: C 72.72 %, H 6.42, N 1.84 % (calculated: C 72.81 %, H 6.38 %, N 1.85 %).

### Preparative Example 2

#### 4,4'-N,N'-Dicyclohexyl-[1,7-di[4-(1,1,3,3-tetramethylbutyl)phenoxy]pervlene]-3,4:9,10-tetracarboxdiimide (4)

##### (i) 4,4'-N,N'-dicyclohexyl-[1,7-di[4-(1,1,3,3-tetramethylbutyl)phenoxy]pervlene]-3,4:9,10-tetracarboxdiimide (2)



The synthesis of the starting material 4,4'-N,N'-dicyclohexyl-[1,7-dibromoperylene-3,4:9,10-tetracarboxdiimide] is described in U. Rohr, P. Schlichting, A. Böhm, M. Groß, K. Meerholz, C. Bräuchle, K. Müllen. *Angew. Chemie* 1998, 110, 1463-1467. In a single necked flask (500 mL) 10.0 g of (14.0 mmol) 4,4'-N,N'-dicyclohexyl-[1,7-dibromoperylene-3,4:9,10-tetracarboxdiimide] were finely suspended in 250 mL of 1-methyl-2-pyrrolidinone (NMP). 3.87 g (23 mmol) of potassium carbonate and 11.55 g (56.0 mmol) of 1,1,3,3-tetramethylbutylphenol were added and the mixture was heated under an argon atmosphere at 100 °C for 20 hours. After cooling to room temperature the reaction mixture was poured under stirring into a mixture of 400 mL 10 % aqueous hydrochloric acid and 600 mL methanol. The precipitate that appeared was filtered, washed extensively with methanol/water (60/40, v/v), dried under vacuum and purified by chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>) to give 12.40 g (92 % yield) of compound (2) as a red solid

m.p. > 355 °C

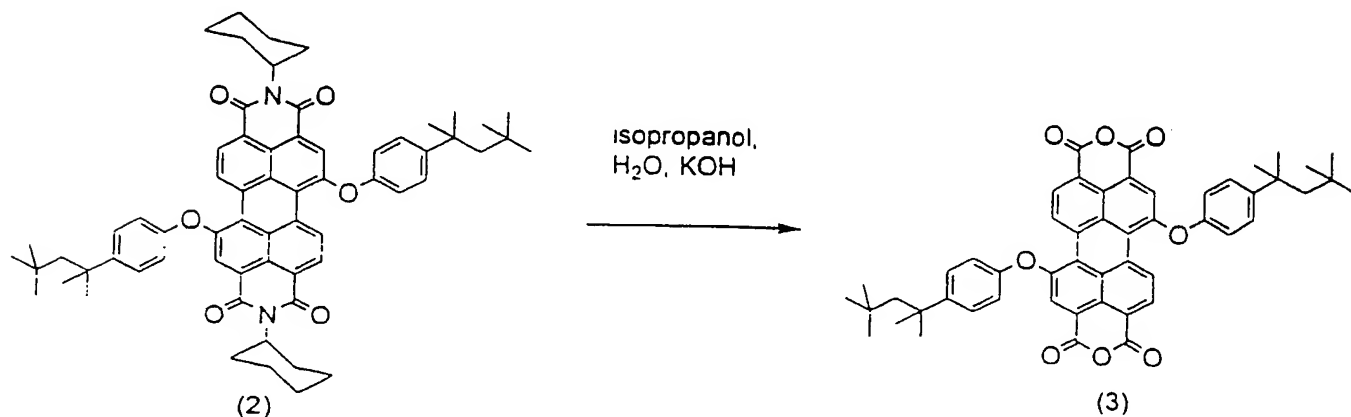
MS (8 kV, FD): m/z = 962 (100 %) [M<sup>+</sup>] (calculated: 962.52)

<sup>1</sup>H-NMR (500 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 25 °C): δ (ppm) = 9.35 (d, 2 H, <sup>3</sup>J(H,H) = 8.50 Hz), 8.47 (d, 2 H, <sup>3</sup>J(H,H) = 8.50 Hz), 8.20 (s, 2 H, <sup>3</sup>J(H,H) =), 7.37 (d, 4 H, <sup>3</sup>J(H,H) = 8.85 Hz), 7.00 (d, 4 H, <sup>3</sup>J(H,H) = 8.85 Hz), 4.87 (m, 2 H), 2.41 (m, 4 H), 1.80 (m, 4 H), 1.67 (s, 4 H), 1.64 (m, 4 H), 1.35 (s, 12 H), 0.72 (s, 18 H).

<sup>13</sup>C-NMR (J-modulated spinecho, 125 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 25 °C): δ (ppm) = 163.96 (C=O), 163.56 (C=O), 155.62 (arom. Cq), 152.63 (arom. Cq), 147.70 (arom. Cq), 133.39 (arom. Cq), 130.28 (arom. CH), 129.29 (arom. Cq), 128.99 (arom. CH), 128.43 (arom. CH), 125.15 (arom. Cq), 124.41 (arom. Cq), 123.97 (arom. CH), 123.75 (arom. Cq), 122.81 (arom. Cq), 119.08 (arom. CH), 57.39 (aliph. CH<sub>2</sub> tert.-octyl), 54.28 (aliph. CH), 38.69 (aliph. Cq), 32.63 (aliph. Cq), 32.15 (aliph. CH<sub>3</sub>), 31.62 (aliph. CH<sub>3</sub>), 29.41 (aliph. CH<sub>2</sub>), 26.83 (aliph. CH<sub>2</sub>), 25.73 (aliph. CH<sub>2</sub>).  
UV/VIS (chloroform solution): λ<sub>max</sub> (ε) = 403.5 nm (9600 L mol<sup>-1</sup> cm<sup>-1</sup>), 510.5 nm (32778 L mol<sup>-1</sup> cm<sup>-1</sup>), 546.5 nm (46780 L mol<sup>-1</sup> cm<sup>-1</sup>)

Fluorescence (chloroform solution, excitation: 510 nm): λ<sub>max</sub> 577 nm

Elemental analysis found: C 79.71 %, H 7.30, N 2.87 % (calculated: C 79.80 %, H 7.32 %, N 2.91 %).

(ii) 1,7-Di[4-(1,1,3,3-tetramethylbutyl)phenoxy]perylene-3,4:9,10-tetracarboxdianhydride (3)

In a single-necked flask (2 L) 7.5 g (7.79 mmol) of 4,4'-N,N'-dicyclohexyl-[1,7-di[4-(1,1,3,3-tetramethylbutyl)phenoxy]perylene]-3,4:9,10-tetracarboxdiimide, prepared as described in step (i) above, were finely suspended in 1 L of 2-propanol. 100 mL of water and 150 g of potassium hydroxide were added and the vigorously stirred mixture was refluxed under an argon atmosphere for 12 hours. After cooling to room temperature, the resulting reaction mixture was poured under stirring into 2.5 L of 10 % hydrochloric acid. The precipitate that appeared was filtered, washed extensively with water and dried under vacuum at 100 °C. The crude product was recrystallised from CH<sub>2</sub>Cl<sub>2</sub>/MeOH to give 6.11 g (98 % yield) of compound (3) as a dark red solid.

m.p. > 350 °C.

MS (8 kV, FD):  $m/z$  = 800.9 (100 %) [ $M^+$ ] (calculated: 800.93).

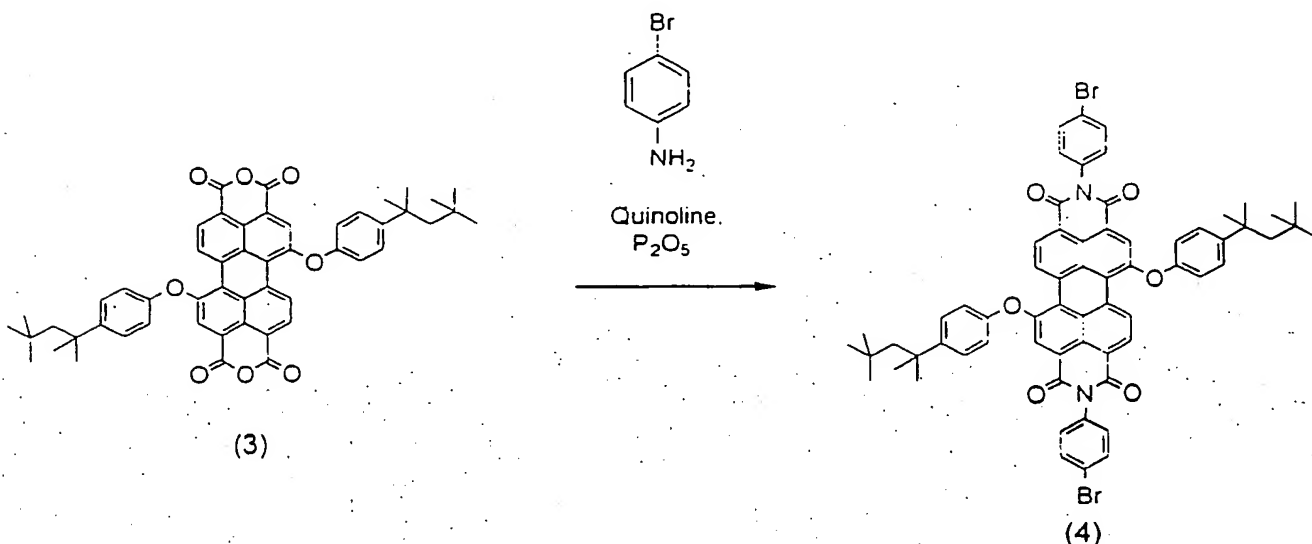
<sup>1</sup>H-NMR (300 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 25 °C):  $\delta$  (ppm) = 9.65 (d, 2 H,  $3J(H,H)$  = 8.50 Hz), 8.60 (d, 2 H,  $3J(H,H)$  = 8.50 Hz), 8.30 (s, 2 H), 7.49 (d, 4 H,  $3J(H,H)$  = 8.60 Hz), 7.09 (d, 4 H,  $3J(H,H)$  = 8.60 Hz), 1.78 (s, 4 H), 1.43 (s, 12 H), 0.82 (s, 18 H).

UV/VIS (chloroform solution):  $\lambda_{max}$  ( $\epsilon$ ) = 512 nm, 547 nm.

Fluorescence (chloroform solution, excitation: 510 nm):  $\lambda_{max}$  = 577 nm.

Elemental analysis found: C 77.81 %, H 6.14 % (calculated: C 77.98 %, H 6.04 %).

(iii) 4,4'-[N,N'-Di-(4-bromophenyl)]-[1,7-di[4-(1,1,3,3-tetramethylbutyl)phenoxy]perylene]-3,4:9,10-tetracarboxdiimide (4)



In a single-necked flask (250 mL) 3.20 g (4 mmol) of 1,7-di[4-(1,1,3,3-tetramethylbutyl)-phenoxy]perylene-3,4:9,10-tetracarboxdianhydride, prepared as described in step (ii) above, were finely suspended in 100 mL of anhydrous quinoline. Then, 7.09 g (40 mmol) of 4-bromoaniline and 0.5 g of phosphorous pentoxide were added and the mixture heated at 180 °C under an argon atmosphere for 12 hours. After cooling to room temperature the mixture was poured into 500 mL of 10 % hydrochloric acid. The precipitate was filtered, washed extensively with a mixture of methanol and water (50/50, v/v) and dried under vacuum at 100 °C. The crude product was purified by column chromatography on silica gel using a mixture of dichloromethane and hexane (80/20, v/v) as the eluent to give 3.90 g (88 % yield) of the title compound as a red solid.

m.p. > 350 °C

MS (8 kV, FD):  $m/z$  = 1106.3 (100 %) [ $M^+$ ] (calculated: 1106.25).

$^1\text{H-NMR}$  (250 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 25 °C):  $\delta$  (ppm) = 9.56 (d, 2 H,  $^3J(\text{H,H})$  = 8.50 Hz), 8.53 (d, 2 H,  $^3J(\text{H,H})$  = 8.50 Hz), 8.21 (s, 2 H), 7.60 (d, 4 H,  $^3J(\text{H,H})$  = 8.50 Hz), 7.39 (d, 4 H,  $^3J(\text{H,H})$  = 8.50 Hz), 7.11 (d, 4 H,  $^3J(\text{H,H})$  = 8.50 Hz), 7.04 (d, 4 H,  $^3J(\text{H,H})$  = 8.50 Hz), 1.67 (s, 4 H), 1.32 (s, 12 H), 0.69 (s, 18 H).

$^{13}\text{C-NMR}$  (J-modulated spinecho, 75 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 25 °C):  $\delta$  (ppm) = 163.44 (C=O), 164.05 (C=O), 156.06 (arom. Cq), 152.20 (arom. Cq), 148.20 (arom. Cq), 134.12 (arom. Cq), 134.05

(arom. Cq), 132.87 (arom. CH), 130.73 (arom. CH), 129.68 (arom. Cq), 129.33 (arom. CH), 128.58 (arom. CH), 125.31 (arom. Cq), 124.01 (arom. Cq), 123.74 (arom. Cq), 123.70 (arom. CH), 123.12 (arom. Cq), 122.14 (arom. CH), 119.40 (arom. CH), 57.34 (aliph. Cq), 38.72 (aliph. Cq), 32.62 (aliph. CH<sub>2</sub>), 32.13 (aliph. CH<sub>3</sub>), 31.67 (aliph. CH<sub>3</sub>).

UV/VIS (chloroform solution):  $\lambda_{\max}(\epsilon) = 405 \text{ nm} (11854 \text{ L mol}^{-1} \text{ cm}^{-1})$ ,  $515 \text{ nm} (39104 \text{ L mol}^{-1} \text{ cm}^{-1})$ ,  $551.5 \text{ nm} (58501 \text{ L mol}^{-1} \text{ cm}^{-1})$ .

Fluorescence (chloroform solution, excitation: 510 nm):  $\lambda_{\max} = 584 \text{ nm}$ .

Elemental analysis found: C 69.22 %, H 5.14 %, N 2.50 % (calculated: C 69.32 %, H 5.09 %, N 2.53 %).

### **Tests to Determine Properties of the Fluorene-Perylene Copolymers of the Invention**

#### **Test Example 1: Measurement of Absolute Photoluminescence Efficiencies**

Absolute photoluminescence efficiencies for some of the copolymers of the invention were measured from thin films spun on quartz substrates following de Mello et al. (see J. C. de Mello, H. F. Wittman, and R. H. Friend, *Adv. Mater.* 1997, 9, 230). An absolute photoluminescence efficiency of approximately 51% was measured for the DM97 copolymer produced in Example 1 above with a peak emission near 545 nm; an absolute photoluminescence efficiency of approximately 40% was measured for the DM87 copolymer produced in Example 2 above with a peak emission near 555 nm; and an absolute photoluminescence efficiency of approximately 33% was measured for the DM77 copolymer produced in Example 3 above with a peak emission peaking near 610 nm. This compares with an absolute photoluminescence efficiency of approximately 56% for the polyfluorene homopolymer which has a vibronically-structured emission centred near 465 nm.

#### **Test Example 2: Measurement of Electroluminescent Emissions**

Thin-film LED structures were constructed using thin-films of copolymers according to the present invention to measure their electroluminescence efficiencies. These were comprised of oxygen plasma-treated ITO-coated glass, a poly(styrene sulfonate)-doped poly(3,4-ethylene dioxythiophene) (PEDOT:PSS) hole injection layer, a polyfluorene-co-perylene emitter, and a Ca-Al cathode. The 70 nm PEDOT:PSS films were spun from a filtered aqueous solution before



heating to 100°C under a nitrogen atmosphere for 30 minutes. Spin-coating was also used to deposit the emissive polymer films of the present invention (approximately 100 nm thickness) from xylene solutions in a nitrogen-filled glove box. The 500Å Ca cathode and 1500Å Al protective layers were deposited by thermal evaporation in vacuum (base pressure  $\sim 5 \times 10^{-6}$  mbar) patterned by a shadow mask. A schematic representation of the resulting PLED device is shown in Figure 1.

Electroluminescence (EL) testing was performed in vacuum ( $\sim 10^{-1}$  mbar) at room temperature. The results are shown in Figure 2. Electrically-stimulated emission spanning the visible range was observed for fluorene-perylene copolymer LEDs produced using the processes described above. Figure 2 shows the EL spectra for the range of fluorene-perylene copolymers in this study. In each case the dominance of the perylene emission and the weak presence of emission from the polyfluorene segments between 400 nm and 460 nm indicates very efficient solid-state energy transfer from the polymer to the chromophores under electrical stimulation. The EL spectra from the DM97 copolymer produced in Example 1 above showed peak emission near 520 nm and CIE x,y coordinates of 0.362, 0.555. The emission from the DM87 copolymer produced in Example 2 above peaked near 558 nm with CIE x,y coordinates of 0.414, 0.519. The emission from the DM77 copolymer produced in Example 3 above showed maximum emission near 600nm and CIE coordinates of 0.590 and 0.365. And, a deep red (CIE x,y of 0.636, 0.338) colour peaking near 675 nm was observed for the DM96 copolymer produced in Example 4 above. This clearly demonstrates the electroluminescence colour-tuning capability of the fluorene-perylene copolymer system.

### **Test Example 3: Measurement of Electroluminescence Efficiencies**

Maximum electroluminescence efficiencies of 1.6 Cd/A and 0.9 Cd/A were observed for LEDs formed according to the procedure described in Test Example 2 above using thin films of copolymers DM97 and DM87 emitting at 558 nm and 520 nm respectively (these were measured from the EL spectra for each device obtained using a calibrated silicon photodiode and the standard photopic response curve). These values compare with green-emitting PEDOT:PSS/PPV and PEDOT:PSS/poly(4,4'-diphenylene diphenylvinylene) devices prepared under similar laboratory conditions where the maximum efficiencies were typically a fraction of a Cd/A (see J. S. Kim et al. *J. Appl. Phys.* 1998, 84, 6859; and T.M. Brown et al, *Appl. Phys. Lett.*

1999, 75, 1679). Efficiencies of 2-7 Cd/A have previously been observed for optimized green-emitting polyfluorene devices with similar anode and cathode materials as in this study (see P. K. H. Ho, D. S. Thomas, R. Friend, and N. Tessler, *Science* 1999, 285, 234; and J. S. Kim, R. H. Friend, and F. Cacialli, *Appl. Phys. Lett.* 1999, 74, 3084).

Figure 3 shows current and luminance versus voltage for an LED, prepared as described in Test example 2 above, incorporating a thin film of the DM87 copolymer produced in Example 2 above, with electroluminescence turn-on near 8 V.

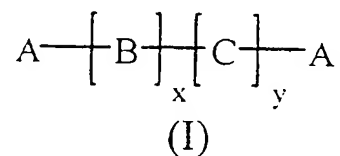
To evaluate the fluorene-terylene copolymers of the present invention PLED structures, analogous to those described in Example 2 above, were also constructed from prior art solution blends of poly-2,7-fluorene and terylene. In the case of green terylene-based blend devices, degradation in the order of 60 seconds (50% initial luminance) was observed for PLEDs operating in vacuum under constant current drive conditions. During this drive period, the emission spectra evolved from that expected from the terylene dye towards that of the polyfluorene. Corresponding with this shift in the emission characteristics, the electrical behavior degraded significantly over this period with rapidly increase in voltage demand. Also, the external quantum efficiencies dropped by over an order of magnitude. It appears that the terylene dye in the emitter layer blend rapidly deactivates optically, possibly through aggregation, and forms non-radiative trap sites. Under similar drive conditions, PLED devices incorporating thin films of the fluorene-terylene copolymers of the present invention show no significant change in the emission spectra over lifetimes of  $>10^3$  seconds. It is very likely that further optimization of device composition, parameters, and fabrication conditions could increase these lifetimes.

It should be noted that the devices in this study are a first demonstration of the colour-tuning capability of the polyfluorene-co-terylene materials system and have not been optimized. It has been shown that careful optimization of anode layer treatment and thickness as well as emitter layer thickness for a particular polymer can dramatically improve the device performance, including such parameters as turn-on voltage and efficiency (see, for example, P. K. H. Ho, D. S. Thomas, R. Friend, and N. Tessler, *Science* 1999, 285, 234; and P. K. H. Ho, M. Granstrom, R. H. Friend, and N. C. Greenham, *Adv. Mater.* 1998, 10, 769). External quantum efficiencies ranging from 0.6% in the green to 0.3% in the red achieved for LEDs based on the

fluorene-terylene copolymers of the present invention demonstrate the potential for efficient emission over the entire spectrum. Electroluminescence lifetime experiments have shown that the copolymers of the present invention can be significantly more stable than the corresponding polyfluorene/dye blends of the prior art in terms of electrical characteristics and emission spectra.

Claims

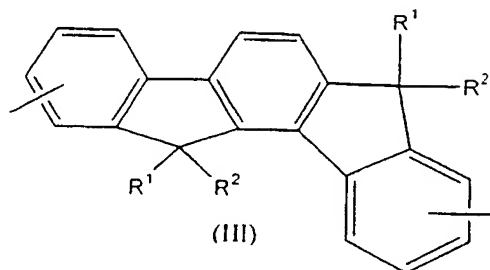
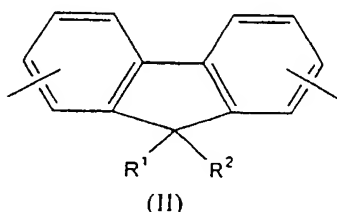
1. A statistical copolymer of the following general formula (I):



wherein:

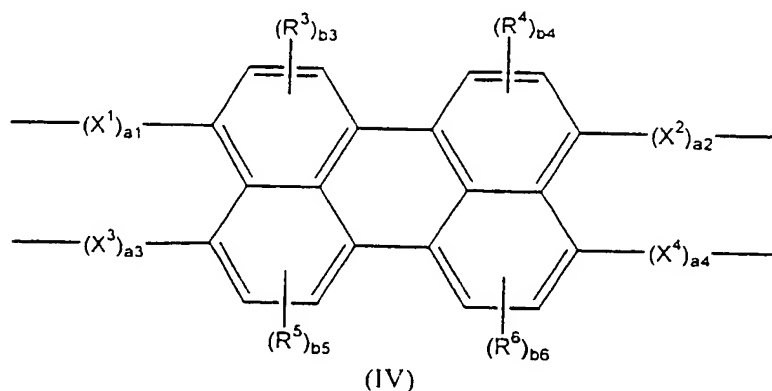
A represents an end-capping unit:

B represents at least one fluorene-containing moiety chosen from moieties of general formulae (II) and (III) below



wherein  $R^1$  and  $R^2$  are the same or different from each other and each is selected from the group consisting of hydrogen atoms, alkyl groups defined below, haloalkyl groups defined below, alkoxy groups defined below, alkoxyalkyl groups defined below, aryl groups defined below and aralkyl groups defined below:

C represents at least one perylene-containing moiety of general formula (IV)



wherein

a1, a2, a3 and a4 are the same or different from each other and each is 0 or 1.

b3, b4, b5 and b6 are the same or different from each other and each is 0, 1 or 2.

X<sup>1</sup>, X<sup>2</sup>, X<sup>3</sup> and X<sup>4</sup> are the same or different from each other and each is a single bond or a linking unit, and

R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> are the same or different from each other and each is selected from the group consisting of alkyl groups defined below, haloalkyl groups defined below, alkoxy groups defined below, alkoxyalkyl groups defined below, aryl groups defined below, aryloxy groups defined below and aralkyl groups defined below; and

the ratio x:y is from 80:20 to 99.9:0.1;

PROVIDED THAT, where A represents an unsubstituted fluorene group, each of b2 to b6 is 0, and either (i) each of a1 and a2 is 0, each of a3 and a4 is 1 and each of X<sup>3</sup> and X<sup>4</sup> is a single bond, or (ii) each of a1 and a4 is 0, each of a2 and a3 is 1 and each of X<sup>2</sup> and X<sup>3</sup> is a single bond, the ratio x:y is from 90:10 to 99.9:0.1;

the alkyl groups in the definitions of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> above are straight or branched-chain alkyl groups having from 1 to 20 carbon atoms;

the haloalkyl groups in the definitions of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> above are alkyl groups as defined above which are substituted by at least one halogen atom;

the alkoxy groups in the definitions of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> above are straight or branched-chain alkoxy groups having from 1 to 20 carbon atoms,

the alkoxyalkyl groups in the definitions of  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  above and aryl groups below are alkyl groups as defined above which are substituted by at least one alkoxy group as defined above;

the aryl groups in the definitions of  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  above and aralkyl and aryloxy groups below are aromatic hydrocarbon groups having from 6 to 14 carbon atoms in one or more rings which may optionally be substituted by at least one substituent selected from the group consisting of nitro groups, cyano groups, amino groups, alkyl groups as defined above, haloalkyl groups as defined above, alkoxyalkyl groups as defined above, aryloxy groups as defined below and alkoxy groups as defined above;

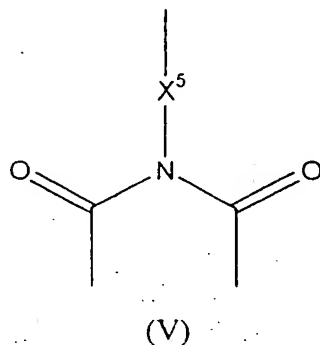
the aryloxy groups in the definitions of  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  above are aryl groups as defined above which are bonded to any oxygen atom; and

the aralkyl groups in the definitions of  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  above are alkyl groups as defined above which are substituted by at least one aryl substituent as defined above.

2. A copolymer of general formula (I) according to claim 1, wherein the ratio x:y is from 90:10 to 99.9:0.1.
3. A copolymer of general formula (I) according to claim 1, wherein the ratio x:y is from 94:6 to 99:1.
4. A copolymer of general formula (I) according to any one of claims 1 to 3, wherein the end capping unit A is a phenyl group, a fluorene group, an indenofluorene group or an end-capping unit which contains a perylene moiety.
5. A copolymer of general formula (I) according to any one of claims 1 to 4 wherein, where  $X^1$ ,  $X^2$ ,  $X^3$  or  $X^4$  is a linking unit, it is selected from the group consisting of arylene groups which are aromatic hydrocarbon groups having from 6 to 14 carbon atoms in one or more rings which may optionally be substituted by at least one substituent selected from the group consisting of nitro groups, cyano groups, amino groups, alkyl groups as defined in claim 1, haloalkyl groups as defined in claim 1, alkoxyalkyl groups as defined in claim 1, aryloxy groups as defined in claim 1 and alkoxy groups as defined in claim 1; straight or branched-chain alkylene

groups having from 1 to 6 carbon atoms; straight or branched-chain alkenylene groups having from 2 to 6 carbon atoms; and straight or branched-chain alkynylene groups having from 1 to 6 carbon atoms.

6. A copolymer of general formula (I) according to any one of claims 1 to 4, wherein  $X^1$  and  $X^2$  together and/or  $X^3$  and  $X^4$  together can represent a linking group of formula (V) below:



wherein  $X^5$  represents an arylene group as defined in claim 5.

7. A copolymer of general formula (I) according to any one of claims 1 to 4, wherein one of  $a_1$  and  $a_2$  is 1 and the other is 0, and the corresponding group of formula  $X^1$  or  $X^2$  is a single bond, and one of  $a_3$  and  $a_4$  is 1 and the other is 0, and the corresponding group of formula  $X^3$  or  $X^4$  is a single bond.

8. A copolymer of general formula (I) according to any one of claims 1 to 4, wherein each of  $a_1$ ,  $a_2$ ,  $a_3$  and  $a_4$  is 1 and  $X^1$  and  $X^2$  together and  $X^3$  and  $X^4$  together each represent a group of formula (V) wherein  $X^5$  represents a phenylene group which may optionally be substituted by at least one substituent selected from the group consisting of alkyl groups as defined in claim 1, haloalkyl groups as defined in claim 1, alkoxyalkyl groups as defined in claim 1, aryloxy groups as defined in claim 1 and alkoxy groups as defined in claim 1.

9. A copolymer of general formula (I) according to claim 8, wherein  $X^5$  is a phenylene group which is substituted by 1 or 2 straight or branched-chain alkyl groups having from 1 to 6 carbon atoms.

10. A copolymer of general formula (I) according to any one of claims 1 to 9, wherein  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  are chosen from the group consisting of alkyl groups as defined in claim 1, alkoxy groups as defined in claim 1 and optionally substituted aryloxy groups as defined in claim 1
11. A copolymer of general formula (I) according to claim 10, wherein  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  are chosen from optionally substituted aryloxy groups as defined in claim 1.
12. A copolymer of general formula (I) according to claim 10, wherein  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  are chosen from phenoxy groups which may optionally be substituted by at least one straight or branched-chain alkyl group having from 1 to 8 carbon atoms or a straight or branched-chain alkoxy group having from 1 to 8 carbon atoms.
13. A copolymer of general formula (I) according to claim 10, wherein  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  are chosen from phenoxy groups which are substituted by a t-butyl group or a 1,1,3,3-tetramethylbutyl group.
14. A copolymer of general formula (I) according to any one of claims 1 to 9, wherein the group of formula (IV) is selected from the group consisting of:
- (i) a group of formula (IV) wherein each of  $b_3$ ,  $b_4$ ,  $b_5$  and  $b_6$  is 0;
  - (ii) a group of formula (IV) wherein one of  $b_3$  and  $b_4$  is 1 and the other is 0 and the corresponding group of formula  $R^3$  or  $R^4$  is a phenoxy group which is substituted by a straight or branched-chain alkyl group having from 1 to 8 carbon atoms, and one of  $b_5$  and  $b_6$  is 1 and the other is 0 and the corresponding group of formula  $R^5$  or  $R^6$  is a phenoxy group which is substituted by a straight or branched-chain alkyl group having from 1 to 8 carbon atoms;
  - (iii) a group of formula (IV) wherein one of  $b_3$  and  $b_4$  is 1 and the other is 0 and the corresponding group of formula  $R^3$  or  $R^4$  is a phenoxy group which is substituted by a t-butyl group or a 1,1,3,3-tetramethylbutyl group, and one of  $b_5$  and  $b_6$  is 1 and the other is 0 and the corresponding group of formula  $R^5$  or  $R^6$  is a phenoxy group which is substituted by a t-butyl group or a 1,1,3,3-tetramethylbutyl group;
  - (iv) a group of formula (IV) wherein each of  $b_3$ ,  $b_4$ ,  $b_5$  and  $b_6$  is 1 and each of  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  is the same or different and each is a phenoxy group which is substituted by a straight or branched-chain alkyl group having from 1 to 8 carbon atoms; and



- (v) a group of formula (IV) wherein each of b3, b4, b5 and b6 is 1 and each of R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> is a phenoxy group which is substituted by a t-butyl group or a 1,1,3,3-tetramethylbutyl group.

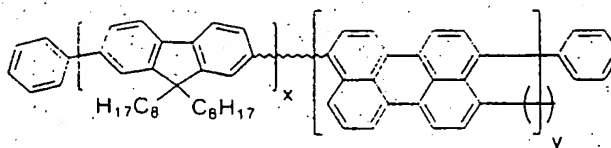
15. A copolymer of general formula (I) according to any one of claims 1 to 14, wherein in the fluorene-containing moieties of formula (II) and formula (III), R<sup>1</sup> and R<sup>2</sup> are the same or different from each other and each is a hydrogen atom or an alkyl group as defined in claim 1.

16. A copolymer of general formula (I) according to any one of claims 1 to 14, wherein in the fluorene-containing moieties of formula (II) and formula (III), each of R<sup>1</sup> and R<sup>2</sup> is a straight or branched-chain alkyl group having from 1 to 10 carbon atoms.

17. A copolymer of general formula (I) according to any one of claims 1 to 14, wherein in the fluorene-containing moieties of formula (II) and formula (III), each of R<sup>1</sup> and R<sup>2</sup> is the same and is a n-octyl group, a 2-ethylhexyl group or a 1,1,3,3-tetramethyl group.

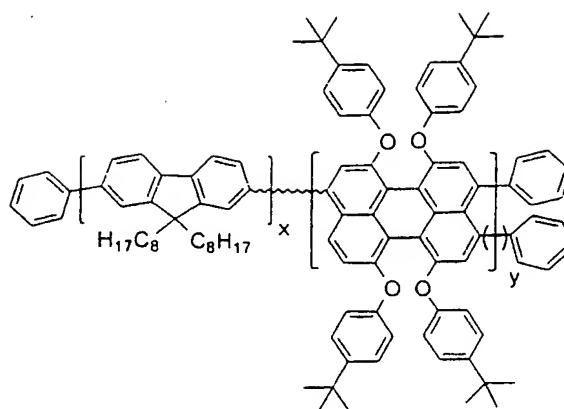
18. A copolymer of general formula (I) according to claim 1 selected from the following group:

(i)



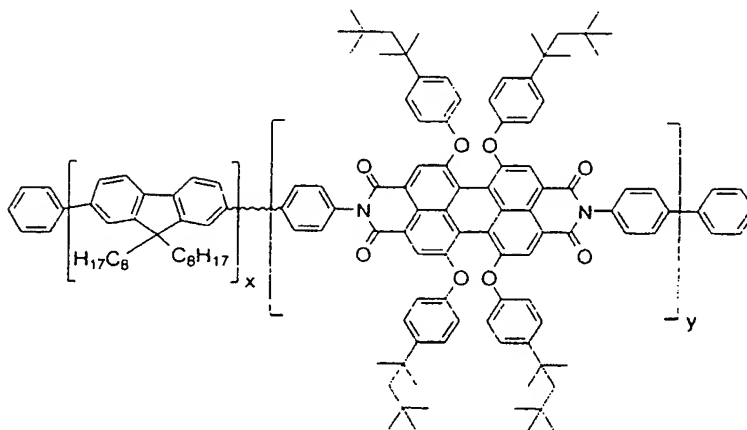
wherein the ratio x:y is from 95:5 to 99.9:0.1;

(ii)



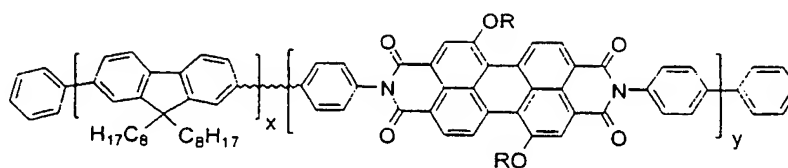
wherein the ratio x:y is from 95:5 to 99.9:0.1;

(iii)



wherein the ratio x:y is from 95:5 to 99.9:0.1;

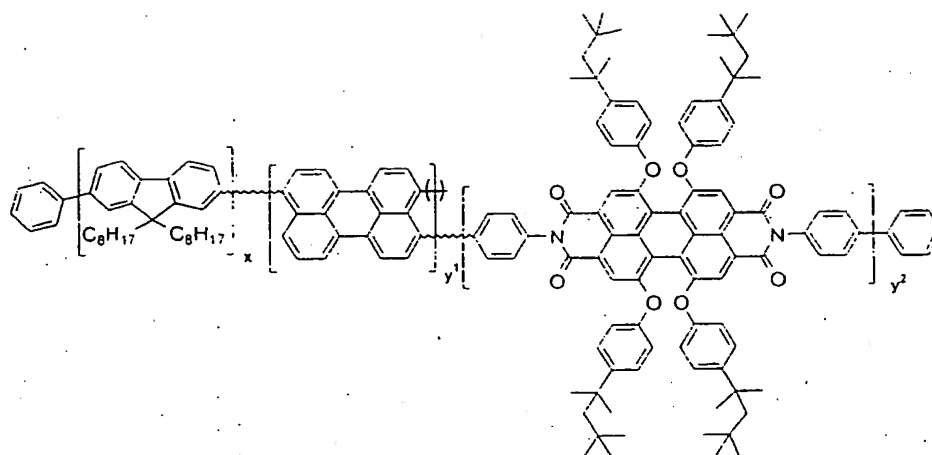
(iv)



wherein R =

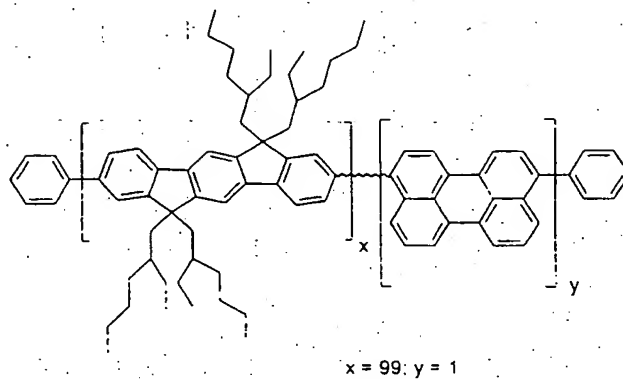
wherein the ratio x:y is from 95:5 to 99.9:0.1;

(v)



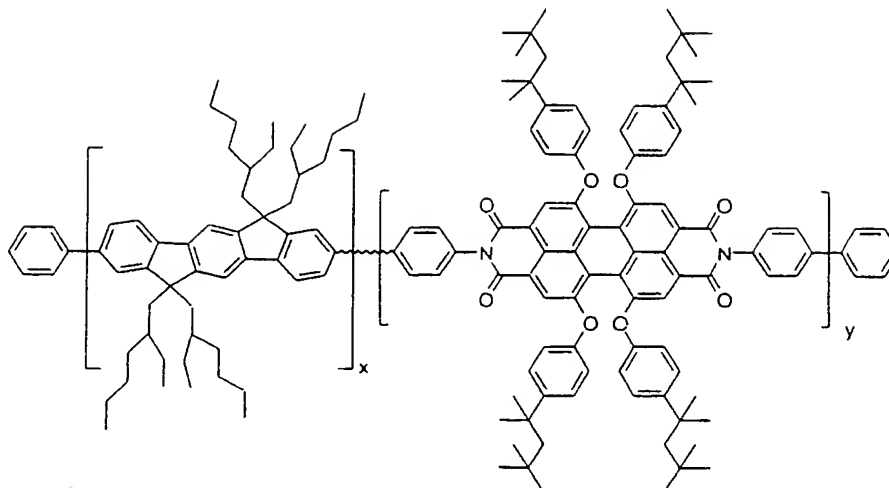
wherein the ratio  $x:y^1:y^2$  is from 94:3:3 to 99.8:0.1:0.1;

(vi)



wherein the ratio  $x:y$  is from 95:5 to 99.9:0.1; and

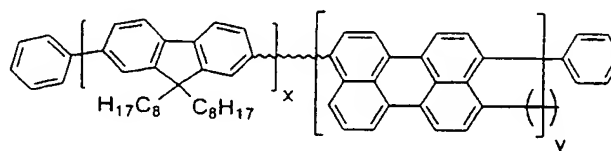
(vii)



wherein the ratio  $x:y$  is from 95:5 to 99.9:0.1.

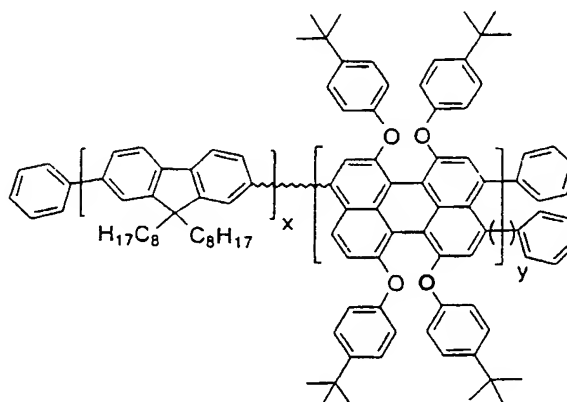
19. A copolymer of general formula (I) according to claim 1 selected from the following group:

(i)



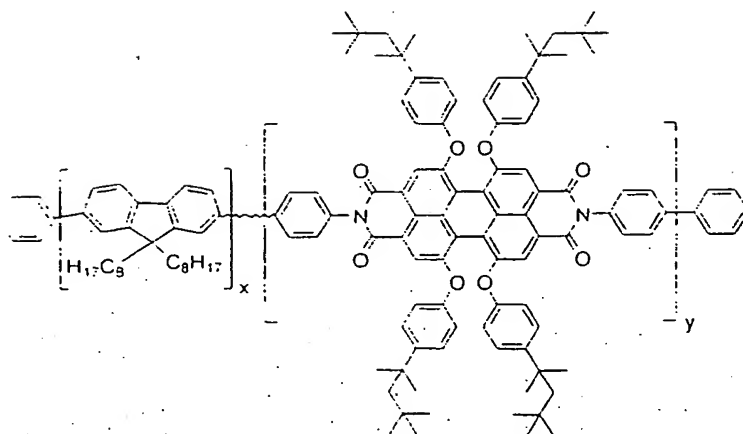
wherein the ratio  $x:y$  is 97:3:

(ii)



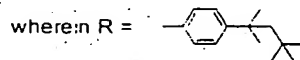
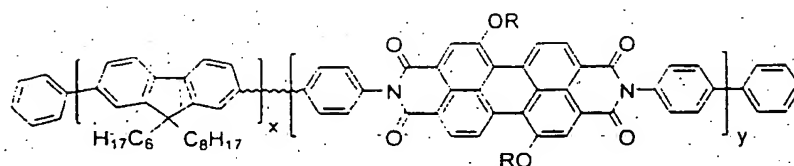
wherein the ratio  $x:y$  is 95:5;

(iii)



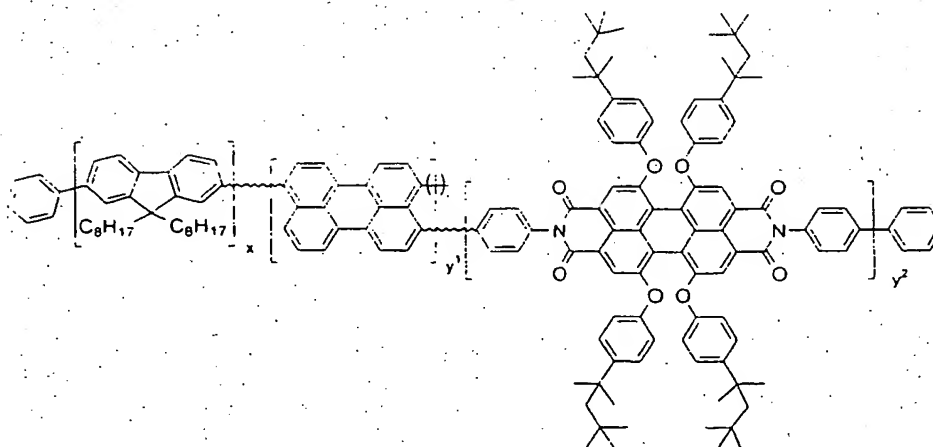
wherein the ratio  $x:y$  is 99:1;

(iv)



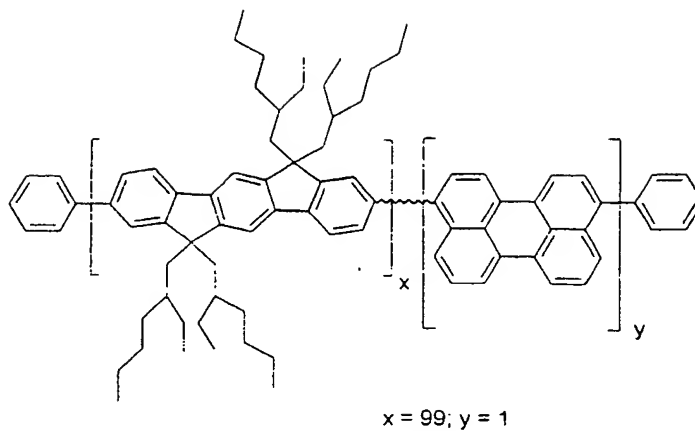
wherein the ratio  $x:y$  is 95:5;

(v)



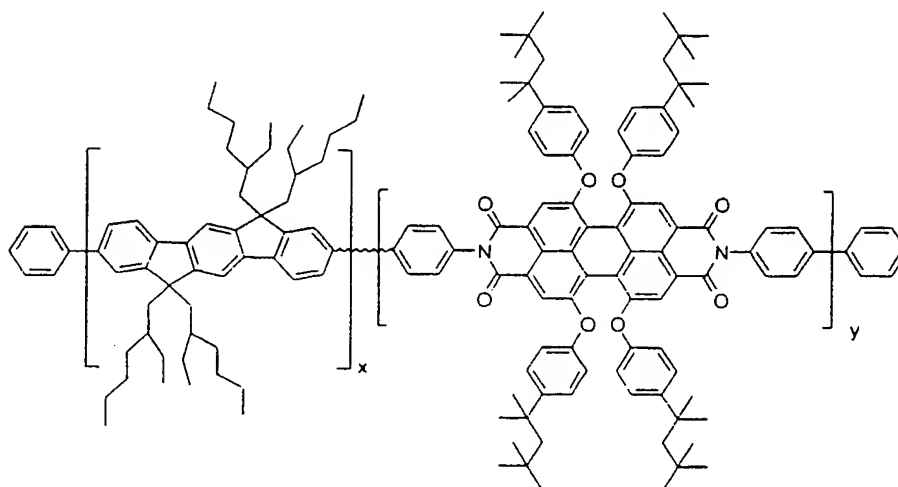
wherein the ratio  $x:y^1:y^2$  is 94:3:3;

(vi)



wherein the ratio  $x:y$  is 99:1: and

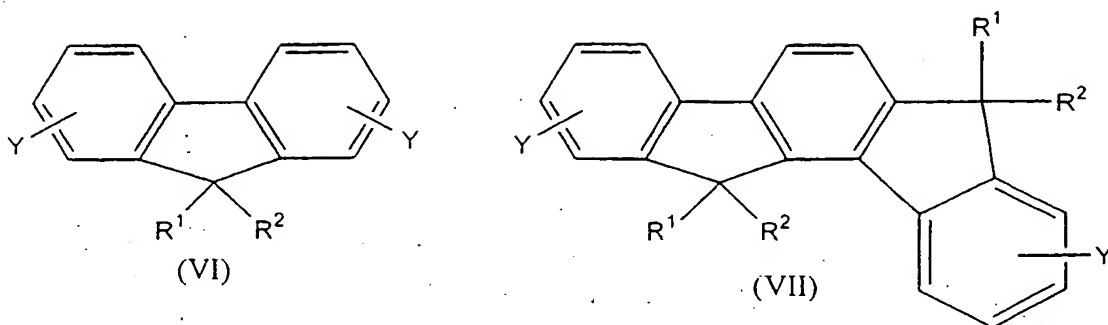
(vii)



wherein the ratio  $x:y$  is 99:1.

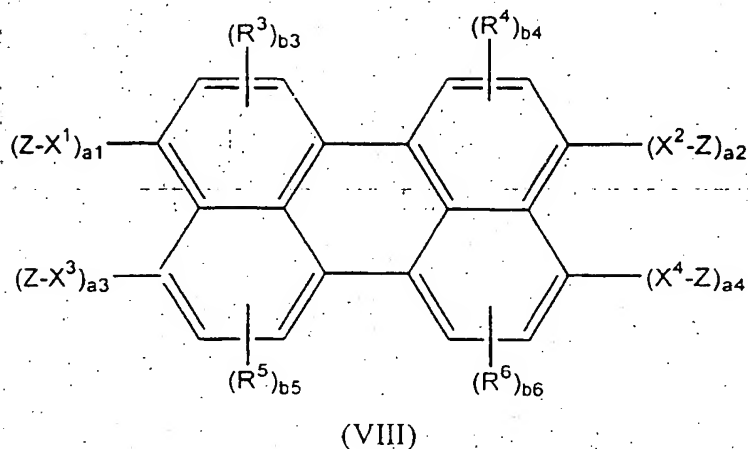
20. A kit for the synthesis of a copolymer of formula (I) according to any one of claims 1 to 19 comprising:

(i) at least one fluorene-containing monomer of general formula (VI) or (VII)



wherein  $R^1$  and  $R^2$  are as defined in claim 1 and Y is a group capable of leaving as a nucleophile;  
and

(ii) at least one perylene-containing monomer of general formula (VIII)



wherein  $a_1$ ,  $a_2$ ,  $a_3$ ,  $a_4$ ,  $b_3$ ,  $b_4$ ,  $b_5$ ,  $b_6$ ,  $X^1$ ,  $X^2$ ,  $X^3$ ,  $X^4$ ,  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  are as defined in claim 1  
and Z is a group capable of leaving as a nucleophile.

21. A kit according to claim 20 wherein each of Y and Z is a bromine atom.

22. An electroluminescent device which incorporates a copolymer of formula (I) according to any one of claim 1 to 20.

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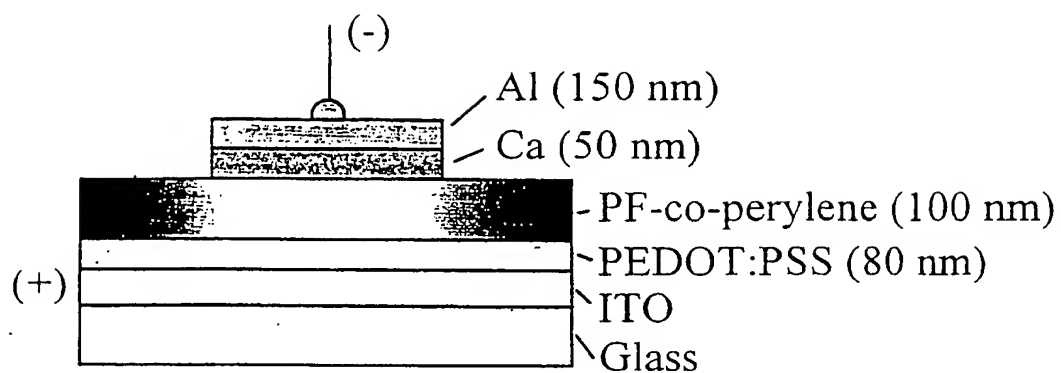


Fig.1

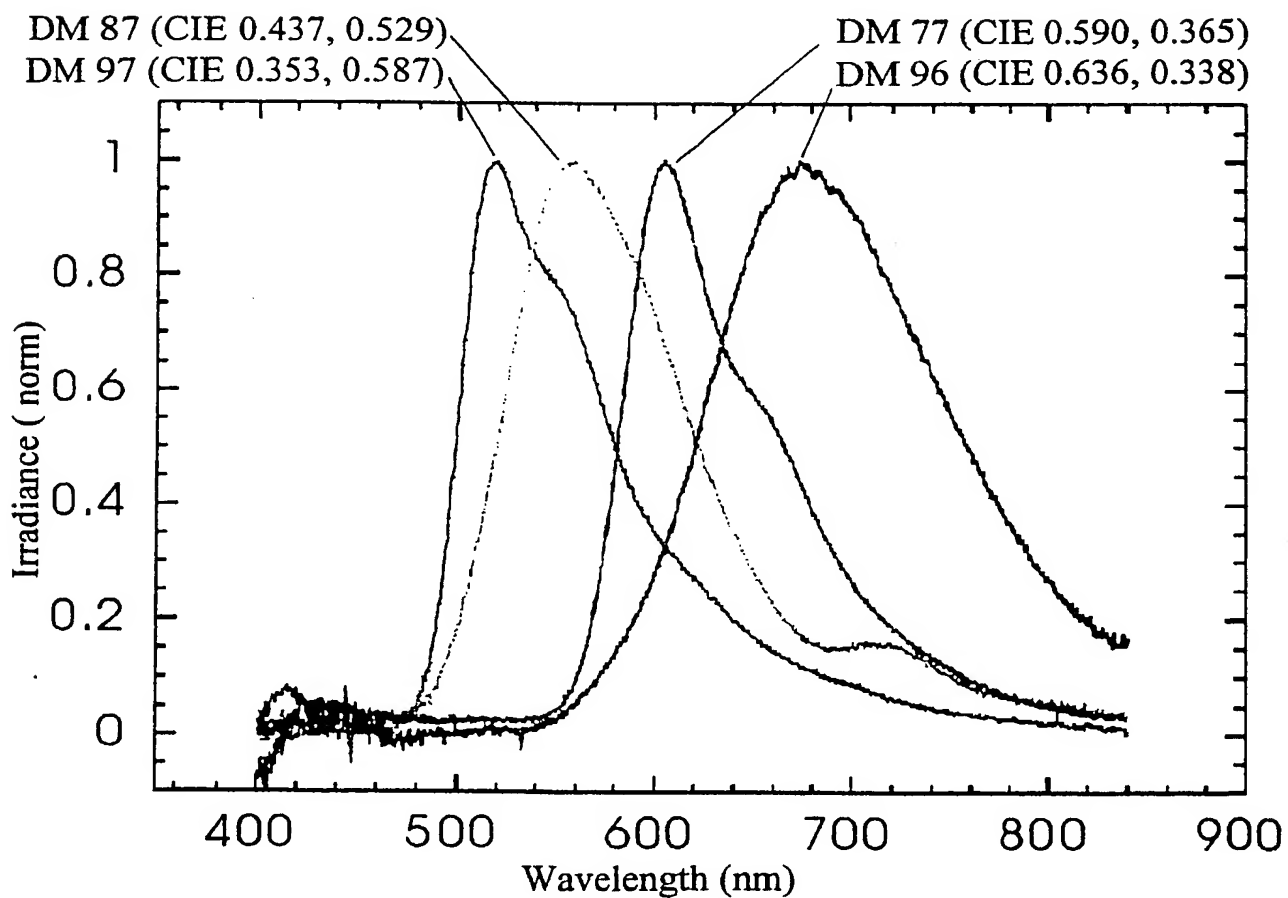


Fig.2

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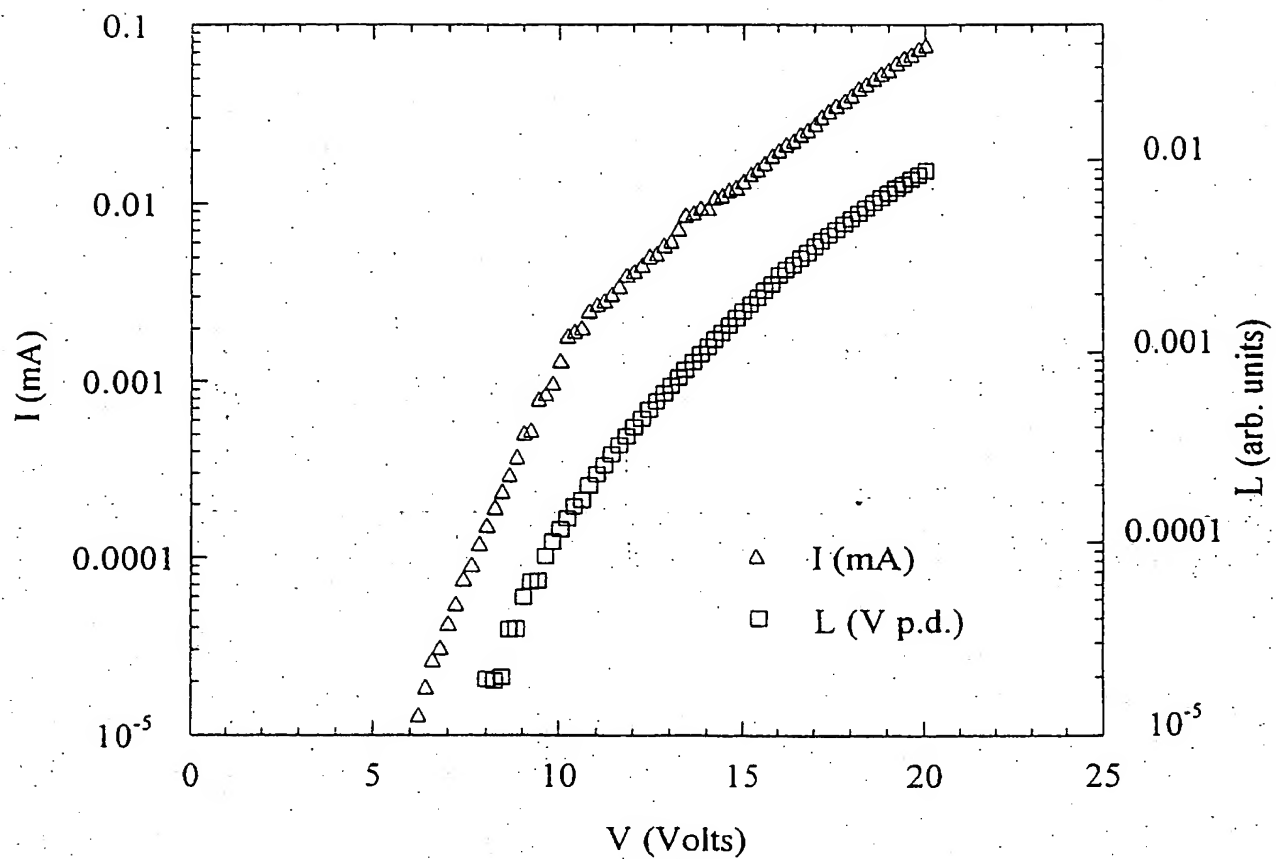


Fig.3

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 00/04594

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C08G61/02 C08G61/10

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KLAERNER G ET AL: "EXCITON MIGRATION AND TRAPPING IN COPOLYMERS BASED ON DIALKYLFLUORENES" ADVANCED MATERIALS, DE, VCH VERLAGSGESELLSCHAFT, WEINHEIM, vol. 11, no. 2, 22 January 1999 (1999-01-22), pages 115-119, XP000877972 ISSN: 0935-9648 figure 4A  --- -/--	1, 2

☒ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

15 February 2001

Date of mailing of the international search report

27/02/2001

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	TASCH S ET AL: "EFFICIENT RED- AND ORANGE-LIGHT-EMITTING DIODES REALIZED BY EXCITATION ENERGY TRANSFER FROM BLUE-LIGHT-EMITTING CONJUGATED POLYMERS" PHYSICAL REVIEW, B. CONDENSED MATTER, US, AMERICAN INSTITUTE OF PHYSICS. NEW YORK, vol. 56, no. 8, PART 02, 15 August 1997 (1997-08-15), pages 4479-4483, XP000742463 ISSN: 0163-1829 figures 3,4 page 4482, column 1, paragraph 3	1, 2
A	US 5 777 070 A (INBASEKARAN MICHAEL ET AL) 7 July 1998 (1998-07-07) example 3	1
A	WO 97 33323 A (UNIAX CORP) 12 September 1997 (1997-09-12) claim 1	1

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 00/04594

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5777070	A	07-07-1998	CN 1276806 T	13-12-2000
			EP 1025142 A	09-08-2000
			WO 9920675 A	29-04-1999
WO 9733323	A	12-09-1997	EP 0885461 A	23-12-1998
			JP 2000506916 T	06-06-2000
			US 5900327 A	04-05-1999

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